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Patent application No.

02405591.5

For the President of the European Patent Office

(signature)

R C van Dijk

THE HAGUE, 01/04/03

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Sheet 2 of the certificate

Application no.: 02405591.5 Date of filing: 11/07/02

Applicant(s):
Ciba Specialty Chemicals Holding Inc.
4057 Basle
SWITZERLAND

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Use of metal complex compounds as oxidation catalysts

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Remarks:

Use of metal complex compounds as oxidation catalysts

The present invention relates to the use, as oxidation catalysts, of metal complex compounds having terpyridine ligands containing at least one quaternised nitrogen atom. The present invention relates also to formulations comprising such metal complex compounds, to novel metal complex compounds and to novel ligands.

The metal complex compounds are used especially for improving the action of peroxides, for example in the treatment of textile material, without at the same time causing any appreciable damage to fibres and dyeings.

Peroxide-containing bleaching agents have been used in washing and cleaning processes for some time. They have an excellent action at a liquor temperature of 90°C and above, but their performance noticeably decreases with lower temperatures. It is known that various transition metal ions, added in the form of suitable salts, or coordination compounds containing such cations activate H_2O_2. In that way it is possible to increase the bleaching action of H_2O_2, or of precursors that release H_2O_2, or of other peroxo compounds, the bleaching action of which is unsatisfactory at lower temperatures. Particularly significant for practical purposes are those combinations of transition metal ions and ligands the peroxide activation of which is manifested in an increased tendency towards oxidation in respect of substrates and not only in a catalase-like disproportionation. The latter activation, which tends rather to be undesirable in the present case, could even impair the bleaching effects of H_2O_2 and its derivatives which are insufficient at low temperatures.

In respect of H_2O_2 activation having effective bleaching action, mononuclear and polynuclear variants of manganese complexes with various ligands, especially with 1,4,7-trimethyl-1,4,7-triazacyclononane and optionally oxygen-containing bridge ligands, are currently regarded as being especially effective. Such catalysts have adequate stability under practical conditions and, with Mn^{n+}, contain an ecologically acceptable metal cation, but their use is unfortunately associated with considerable damage to dyes and fibres.

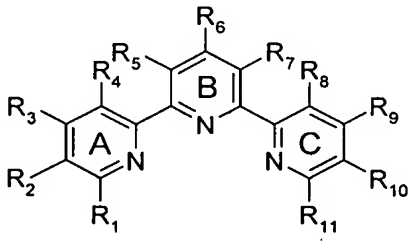
The aim of the present invention was accordingly to provide improved metal complex catalysts for oxidation processes which fulfil the above demands and, especially, improve the

action of peroxide compounds in an extremely wide range of fields of use without giving rise to any appreciable damage.

The invention accordingly relates to the use of metal complex compounds of formula (1)

$$[L_nMe_mX_p]^zY_q \qquad (1),$$

wherein Me is manganese, titanium, iron, cobalt, nickel or copper,
X is a coordinating or bridging radical,
n and m are each independently of the other an integer having a value of from 1 to 8,
p is an integer having a value of from 0 to 32,
z is the charge of the metal complex,
Y is a counter-ion,
q = z/(charge Y), and
L is a ligand of formula (2)



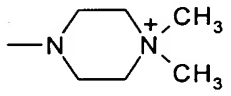
(2),

wherein
R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen; unsubstituted or substituted C_1-C_{18}alkyl or aryl; cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N[(C_1$-C_6alkylene$)-NR_{14}R_{15}]_2$, $-N(R_{13})-(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$, $-N[(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}]_2$, $-N(R_{13})-N-R_{14}R_{15}$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen

atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms,
with the proviso that

(i) at least one of the substituents $R_1 - R_{11}$ contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn(II), $R_1 - R_5$ and $R_7 - R_{11}$ are hydrogen and R_6 is



as catalysts for oxidation reactions.

The mentioned C_1-C_{18}alkyl radicals are generally, for example, straight-chain or branched alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl or straight-chain or branched pentyl, hexyl, heptyl or octyl. Preference is given to C_1-C_{12}alkyl radicals, especially C_1-C_8alkyl radicals and more especially C_1-C_4alkyl radicals. The mentioned alkyl radicals may be unsubstituted or substituted, for example by hydroxyl, C_1-C_4alkoxy, sulfo or by sulfato, especially by hydroxyl. The corresponding unsubstituted alkyl radicals are preferred. Very special preference is given to methyl and ethyl, especially methyl.

Examples of aryl radicals that generally come into consideration are phenyl or naphthyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy, wherein the amino groups may or may not be quaternised. Preferred substituents are C_1-C_4alkyl, C_1-C_4alkoxy, phenyl and hydroxy.
Special preference is given to the corresponding phenyl radicals.

The mentioned C_1-C_6alkylene groups are generally, for example, straight-chain or branched alkylene radicals, such as methylene, ethylene, n-propylene or n-butylene. The mentioned alkylene radicals may be unsubstituted or substituted, for example by hydroxyl or by C_1-C_4alkoxy.

Halogen is generally preferably chlorine, bromine or fluorine, special preference being given to chlorine.

Examples of cations that generally come into consideration are alkali metal cations, such as lithium, potassium and especially sodium, alkaline earth metal cations, such as magnesium and calcium, and ammonium cations. The corresponding alkali metal cations, especially sodium, are preferred.

Suitable metal ions for Me are, for example, manganese in oxidation states II-V, titanium in oxidation states III and IV, iron in oxidation states I to IV, cobalt in oxidation states I to III, nickel in oxidation states I to III and copper in oxidation states I to III, with special preference being given to manganese, especially manganese in oxidation states II to IV, preferably in oxidation state II. Also of interest are titanium IV, iron II-IV, cobalt II-III, nickel II-III and copper II-III, especially iron II-IV.

For the radical X there come into consideration, for example, CH_3CN; H_2O; F^-; Cl^-; Br^-; HOO^-; O_2^{2-}; O^{2-}; $R_{17}COO^-$; $R_{17}O^-$; $LMeO^-$ or $LMeOO^-$, wherein R_{17} is hydrogen, $-SO_3C_1$-C_4alkyl or unsubstituted or substituted C_1-C_{18}alkyl or aryl, wherein C_1-C_{18}alkyl, aryl, L and Me have the definitions and preferred meanings given hereinabove and hereinbelow. R_{17} is especially hydrogen; C_1-C_4alkyl; sulfophenyl or phenyl, more especially hydrogen.

As counter-ion Y there come into consideration, for example, $R_{17}COO^-$; ClO_4^-; BF_4^-; PF_6^-; $R_{17}SO_3^-$; $R_{17}SO_4^-$; SO_4^{2-}; NO_3^-; F^-; Cl^-; Br^- and I^-, wherein R_{17} is hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl. R_{17} as C_1-C_{18}alkyl or aryl has the definitions and preferred meanings given hereinabove and hereinbelow. R_{17} is especially hydrogen; C_1-C_4alkyl; phenyl or sulfophenyl, more especially hydrogen or 4-sulfophenyl. The charge of the counter-ion Y is accordingly preferably 1- or 2-, especially 1-.
Y may also be a conventional organic counter-ion such as, for example, citrate, oxalate or tartrate.

n is preferably an integer having a value of from 1 to 4, preferably 1 or 2 and especially 1.

m is preferably an integer having a value of 1 or 2, especially 1.

p is preferably an integer having a value of from 0 to 4, especially 2.

z is preferably an integer having a value of from 8- to 8+, especially from 4- to 4+ and more especially from 0 to 4+. z is very especially the number 0.

q is preferably an integer from 0 to 8, especially from 0 to 4 and is more especially the number 0.

R_{12} is preferably hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above. R_{12} is especially hydrogen, an alkali metal cation, alkaline earth metal cation or ammonium cation, C_1-C_4alkyl or phenyl, more especially hydrogen or an alkali metal cation, alkaline earth metal cation or ammonium cation.

R_{13} is preferably hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above. R_{13} is especially hydrogen, C_1-C_4alkyl or phenyl, more especially hydrogen or C_1-C_4alkyl, preferably hydrogen. Examples of the radical of the formula -OR_{13} that may be mentioned include hydroxyl and C_1-C_4alkoxy, such as methoxy and especially ethoxy.

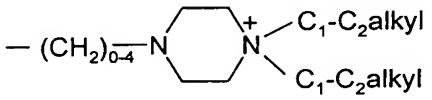
When R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring, the ring is preferably an unsubstituted or C_1-C_4alkyl-substituted pyrrolidine, piperidine, piperazine, morpholine or azepane ring, wherein the amino groups may or may not be quaternised, with preference being given to those nitrogen atoms not directly bonded to any of the three pyridine rings A, B or C being quaternised.
The piperazine ring may be substituted, for example at the nitrogen atom not linked to the phenyl radical, by one or two unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical(s).
In addition, R_{14}, R_{15} and R_{16} are preferably hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above. Special preference is given to hydrogen, unsubstituted or hydroxyl-substituted C_1-C_4alkyl or phenyl, especially hydrogen or unsubstituted or hydroxyl-substituted C_1-C_4alkyl, preferably hydrogen.

Preference is given to ligands of formula (2) wherein R_6 is not hydrogen.

R_6 is preferably C_1-C_{12}alkyl; phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy; cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-N-$R_{14}R_{15}$ or $-N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, piperazine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised.

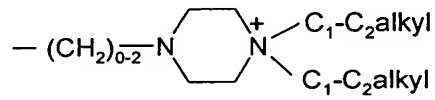
R_6 is especially phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, phenyl or by hydroxyl; cyano; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_4alkyl or phenyl; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_4alkyl or phenyl; $-N(CH_3)$-NH_2 or $-NH$-NH_2; amino; N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, wherein the nitrogen atoms, especially the nitrogen atoms not bonded to any of the three pyridine rings A, B or C, may or may not be quaternised; N-mono- or N,N-di-C_1-C_4alkyl-$N^{\oplus}R_{14}R_{15}R_{16}$ unsubstituted or substituted by hydroxy in the alkyl moiety, wherein R_{14}, R_{15} and R_{16} are each independently of the others hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, piperazine, morpholine or azepane ring which is unsubstituted or substituted by at least one C_1-C_4alkyl radical or by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised; or N-mono- or N,N-di-C_1-C_4alkyl-$NR_{14}R_{15}$ unsubstituted or substituted by hydroxy in the alkyl moiety, R_{14} and R_{15} therein being as defined above.

R_6 is very especially C_1-C_4alkoxy; hydroxy; phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, phenyl or by hydroxy; hydrazino; amino; N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, wherein the nitrogen atoms, especially the nitrogen atoms not bonded to any of the three pyridine rings A, B or C, may or may not be quaternised; or a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by one or two unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical(s), in which ring the nitrogen atom may be quaternised.
As a likewise very especially preferred radical R_6 there may be mentioned



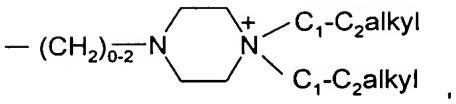
wherein the ring and the two alkyl groups may be unsubstituted or may be additionally substituted.

Especially important as radicals R_6 are C_1-C_4alkoxy; hydroxy; hydrazino; amino; N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, wherein the nitrogen atoms, especially the nitrogen atoms not bonded to any of the three pyridine rings A, B or C, may or may not be quaternised; or a pyrrolidine, piperidine, piperazine, morpholine or azepane ring which is unsubstituted or substituted by at least one C_1-C_4alkyl radical, in which ring the nitrogen atoms may or may not be quaternised.
As a further especially important example of R_6 there may be mentioned the radical



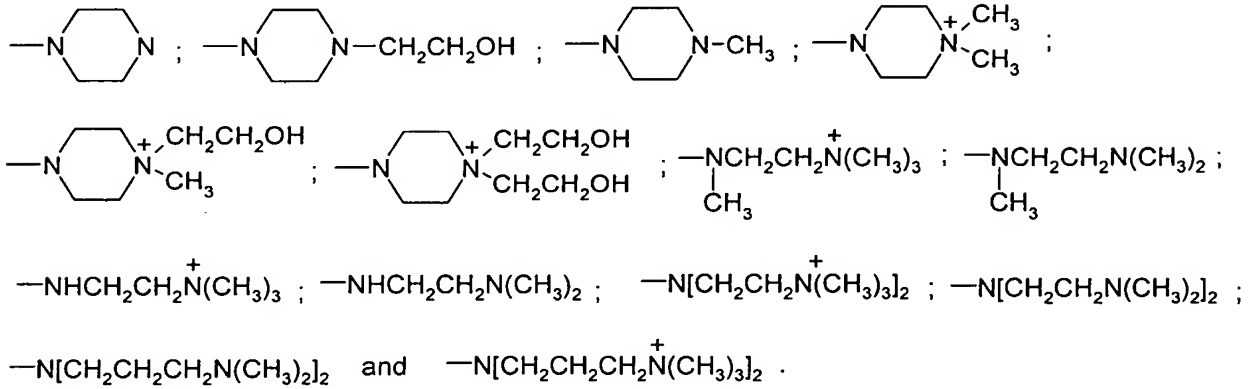
wherein the ring and the two alkyl groups may be unsubstituted or may be additionally substituted.

Very especially important as radicals R_6 are C_1-C_4alkoxy; hydroxy; N-mono- or N,N-di-C_1-C_4alkylamino substituted by hydroxy in the alkyl moiety, wherein the nitrogen atoms, especially the nitrogen atoms not bonded to any of the three pyridine rings A, B or C, may or may not be quaternised; or a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by at least one C_1-C_4alkyl radical, wherein the amino groups may or may not be quaternised.
As a further very especially important example of R_6 there may be mentioned the radical



wherein the ring and the two alkyl groups may be unsubstituted or may be additionally substituted.

As examples of the radical R_6 there may be mentioned especially



Hydroxyl is of special interest in this context.

The preferred meanings indicated above for R_6 apply also to R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11}, but those radicals may additionally denote hydrogen.

In accordance with one embodiment of the present invention, R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11} are hydrogen and R_6 is a radical other than hydrogen having the definitions and preferred meanings indicated above.
In accordance with a further embodiment of the present invention, R_1, R_2, R_4, R_5, R_7, R_8, R_{10} and R_{11} are hydrogen and R_3, R_6 and R_9 are radicals other than hydrogen having the definitions and preferred meanings indicated above for R_6.

A likewise preferred use of metal complex compounds of formula (1) as catalysts for oxidation reactions is characterised in that at least one of the substituents $R_1 - R_{11}$, preferably R_3, R_6 and/or R_9, is one of the following radicals
-(C_1-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$,
-$N[(C_1$-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or

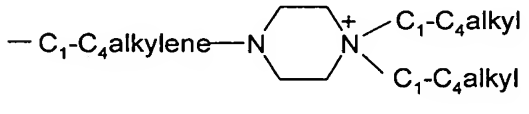
substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; or
$-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N(R_{13})-(C_1$-C_6alkylene$)-NR_{14}R_{15}$,
$-N[(C_1$-C_6alkylene$)-NR_{14}R_{15}]_2$ or $-N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

A likewise more preferred use of metal complex compounds of formula (1) as catalysts for oxidation reactions is characterised in that at least one of the substituents $R_1 - R_{11}$, preferably R_3, R_6 and/or R_9, is one of the following radicals
$-(C_1$-C_4alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(C_1$-C_4alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$,
$-N[(C_1$-C_4alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}]_2$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is hydrogen or unsubstituted or substituted C_1-C_{12}alkyl or aryl and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{12}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms; or
$-NR_{14}R_{15}$, $-(C_1$-C_4alkylene$)-NR_{14}R_{15}$, $-N(R_{13})-(C_1$-C_4alkylene$)-NR_{14}R_{15}$,
$-N[(C_1$-C_4alkylene$)-NR_{14}R_{15}]_2$ or $-N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are each independently of the other hydrogen or unsubstituted or substituted C_1-C_{12}alkyl or aryl and R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

A likewise especially preferred use of metal complex compounds of formula (1) is characterised in that at least one of the substituents $R_1 - R_{11}$, preferably R_3, R_6 and/or R_9, is one of the following radicals
$-(C_1$-C_4alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$,
$-N[(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}]_2$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or

substituted C_1-C_{12}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms; or
$-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N(R_{13})-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N[(C_1$-C_6alkylene$)-NR_{14}R_{15}]_2$ or $-N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, in which ring the nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

A likewise important use of metal complex compounds of formula (1) is characterised in that at least one of the substituents $R_1 - R_{11}$, preferably R_3, R_6 and/or R_9, is a radical



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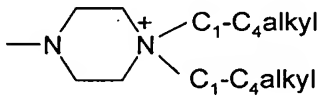

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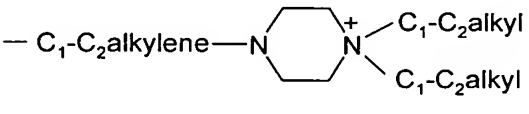
wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each of which independently of the other is unbranched or branched, may be unsubstituted or substituted.
The piperazine ring may also be unsubstituted or substituted.

A likewise especially important use of metal complex compounds of formula (1) is characterised in that at least one of the substituents $R_1 - R_{11}$, preferably R_3, R_6 and/or R_9, is a radical



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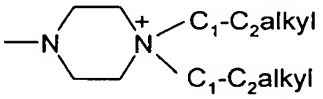

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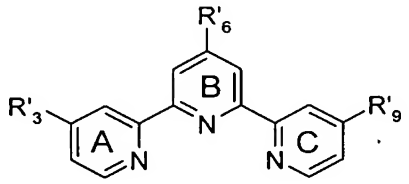
wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each independently of the other, may be unsubstituted or substituted.

The piperazine ring may also be unsubstituted or substituted.

Preferred ligands L are those of formula (3)

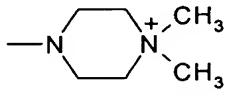


(3),

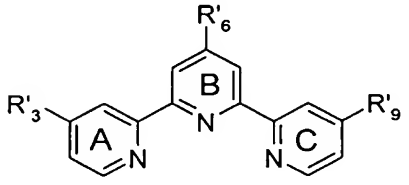
wherein R'_3, R'_6 and R'_9 have the definitions and preferred meanings indicated above for R_6, it being possible in addition for R'_3 and R'_9 to be hydrogen, likewise with the proviso that

(i) at least one of the substituents R'_3, R'_6 and/or R'_9 contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn(II), R'_3 and R'_9 are hydrogen and R'_6 is



Ligands L to which greater preference is given are those of formula (3)



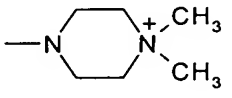
(3),

wherein R'_3, R'_6 and R'_9 have the definitions and preferred meanings indicated above for R_6, it being possible in addition for R'_3 and R'_9 to be hydrogen, with the proviso that

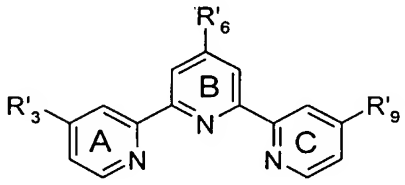
(i) at least one of the substituents R'_3, R'_6 und R'_9 is a radical -(C_1-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N[(C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the

nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; or $-NR_{14}R_{15}$, $-(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}$, $-N(R_{13})\text{-}(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}$, $-N[(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}]_2$ or $-N(R_{13})\text{-}N\text{-}R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted $C_1\text{-}C_4$alkyl and/or substituted $C_1\text{-}C_4$alkyl radical and which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn(II), R'_3 and R'_9 are hydrogen and R'_6 is



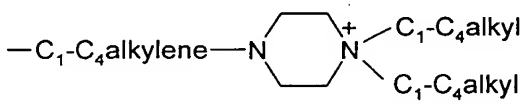
Ligands L to which even greater preference is given are those of formula (3)



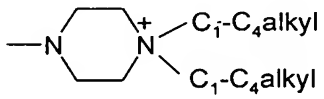
(3),

wherein R'_3, R'_6 and R'_9 have the definitions and preferred meanings indicated above for R_6, it being possible in addition for R'_3 and R'_9 to be hydrogen, with the proviso that

(i) at least one of the substituents R'_3, R'_6 and R'_9 is one of the radicals



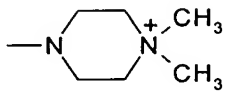
or



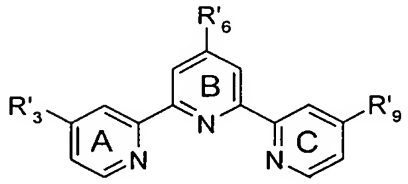
,

wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each of which independently of the other is unbranched or branched, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn(II), R'_3 and R'_9 are hydrogen and R'_6 is



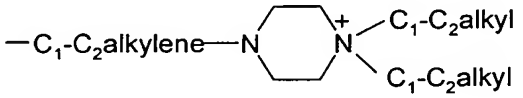
Ligands L to which special preference is given are those of formula (3)



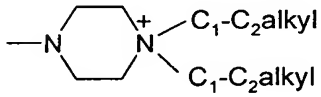
(3),

wherein R'_3, R'_6 and R'_9 have the definitions and preferred meanings indicated above for R_6, it being possible in addition for R'_3 and R'_9 to be hydrogen, with the proviso that

(i) at least one of the substituents R'_3, R'_6 and R'_9 is one of the radicals

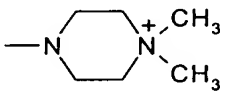


or



wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each of which independently of the other is unbranched or branched, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted, and that

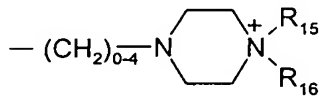
(ii) Y is neither I^- nor Cl^- if Me is Mn(II), R'_3 and R'_9 are hydrogen and R'_6 is



R'_3, R'_6 and R'_9 preferably are, each independently of the others, phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, phenyl or by hydroxyl; cyano; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_4alkyl or phenyl; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_4alkyl or phenyl;

-$N(CH_3)$-NH_2 or -NH-NH_2; amino; N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, wherein the nitrogen atoms, especially the nitrogen atoms not bonded to any of the three pyridine rings A, B or C, may or may not be quaternised; N-mono- or N,N-di-C_1-C_4alkyl-$N^{\oplus}R_{14}R_{15}R_{16}$ unsubstituted or substituted by hydroxy in the alkyl moiety, wherein R_{14}, R_{15} and R_{16} are each independently of the others hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, piperazine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised; or N-mono- or N,N-di-C_1-C_4alkyl-$NR_{14}R_{15}$ unsubstituted or substituted by hydroxy in the alkyl moiety, R_{14} and R_{15} therein being as defined above.

R'_3, R'_6 and R'_9 may especially be a radical



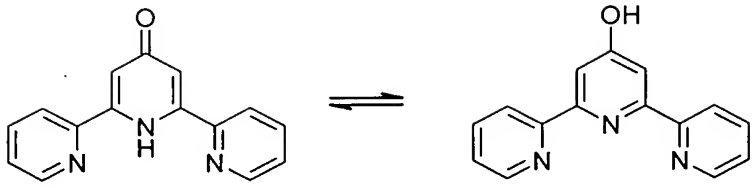
wherein R_{15} and R_{16} are as defined above and the ring is unsubstituted or substituted. Likewise, R'_3 and R'_9 may also be hydrogen.

Preference is given to compounds in which 1 quaternised nitrogen atom is present. Preference is likewise given to compounds wherein 2 or 3 quaternised nitrogen atoms are present.

Special preference is given to compounds wherein no quaternised nitrogen atom is directly bonded to any of the pyridine rings A, B or C.

The metal complex compounds of formula (1) can be obtained analogously to known processes. They are obtained in a manner known *per se* by reacting at least one ligand of formula (2) in the desired molar ratio with a metal compound, especially a metal salt, such as the chloride, to form the corresponding metal complex. The reaction is carried out, for example, in a solvent, such as water or a lower alcohol, such as ethanol, at a temperature of, for example, from 10 to 60°C, especially at room temperature.

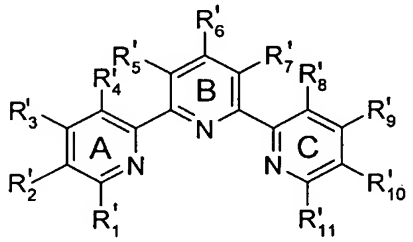
Ligands of formula (2) that are substituted by hydroxyl can also be formulated as compounds having a pyridone structure in accordance with the following scheme:



terpyridin-4'-one structure terpyridin-4'-ol structure

Generally, therefore, hydroxyl-substituted terpyridines are also to be understood as including those having a corresponding pyridone structure.

The ligands of formula (2) can be prepared in a manner known *per se*. For that purpose, for example, a compound of formula (4)



(4),

which contains no quaternised nitrogen atoms and

wherein R'_1– R'_{11} may have the definitions and preferred meanings indicated for the substituents R_1 – R_{11} with the exception of quaternised nitrogen atoms and with the proviso that at least one of the substituents R'_1 – R'_{11} is halogen, NO_2 or OR_{18}, wherein R_{18} is $-SO_2CH_3$ or tosylate,

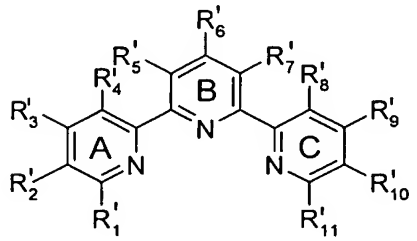
is reacted with a corresponding stoichiometric amount of a compound of formula (5)

HNR (5),

wherein R has one of the meanings of R_1 – R_{11} with the proviso that it contains a quaternisable nitrogen group not directly bonded to any of the three pyridine rings A, B or C. The stoichiometric amount of the compound of formula (5) is governed by the number of halogen atoms, NO_2 or OR_{18} groups that are present in the compound of formula (4), R_{18} therein being as defined above. Preference is given to compounds of formula (4) which have 1, 2 or 3 such radical(s).

In a further step, the reaction product of compounds (4) and (5) is quaternised using known quaternising agents such as, for example, especially methyl iodide or dimethyl sulfate so that at least one quaternised nitrogen atom is present.
It has now been found that, for the purpose of accelerated replacement of halide by amine on the terpyridine structure, catalytic amounts of non-transition-metal salts such as, for example, zinc(II) salts can also be used, which substantially simplifies the reaction procedure and work-up.

The present invention relates also to compounds of formula (4)



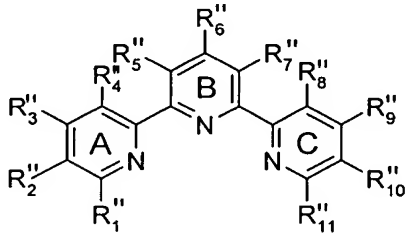
(4) ,

wherein
$R'_1 - R'_{11}$ may have the definitions and preferred meanings indicated for the substituents $R_1 - R_{11}$ with the exception of quaternised nitrogen atoms and with the proviso that

(i) at least one of the substituents $R'_1 - R'_7$ is halogen, NO_2 or OR_{18}, wherein R_{18} is $-SO_2CH_3$ or tosylate, and

(ii) the substituents R'_8 - R'_{11} are neither halogen nor NO_2 or R_{18}, wherein R_{18} is as defined under (i).

The present invention relates also to compounds of formula (4a), which are reaction products of the compounds of formula (4) with the compounds of formula (5),



(4a) ,

wherein $R''_1 - R''_{11}$ may have the definitions and preferred meanings indicated for the substituents $R_1 - R_{11}$ with the exception of quaternised nitrogen atoms and with the proviso that

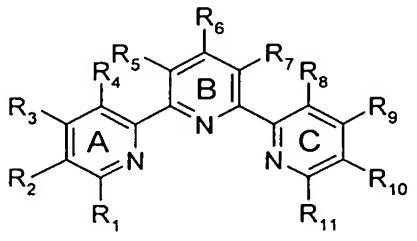
at least one of the substituents $R''_1 - R''_7$ contains a quaternisable nitrogen group which is not directly bonded to either of the two pyridine rings A and/or B.

The compounds of formula (4) can be prepared by processes known *per se*. These processes are described in K. T. Potts, D. Konwar, J. Org. Chem. 2000, 56, 4815-4816, E. C. Constable, M. D. Ward, J. Chem. Soc. Dalton Trans. 1990, 1405-1409, E. C. Constable, A. M. W. Cargill Thompson, New. J. Chem. 1992, 16, 855-867, G. Lowe *et al.*, J. Med. Chem., 1999, 42, 999-1006, E.C. Constable, P. Harveson, D.R. Smith, L. Whall, Polyhedron 1997, 16, 3615-3623, R. J. Sundberg, S. Jiang, Org. Prep. Proced. Int. 1997, 29, 117-122, T. Sammakia, T. B. Hurley, J. Org. Chem. 2000, 65, 974-978 and J. Limburg *et al.*, Science 1999, 283, 1524-1527.

The present invention relates also to novel metal complex compounds of formula (1a)

$$[L_nMe_mX_p]^zY_q \qquad (1a),$$

wherein Me is manganese, titanium, iron, cobalt, nickel or copper,
X is a coordinating or bridging radical,
n and m are each independently of the other an integer having a value of from 1 to 8,
p is an integer having a value of from 0 to 32,
z is the charge of the metal complex,
Y is a counter-ion,
q = z/(charge Y), and
L is a ligand of formula (2a)



(2a),

wherein

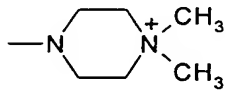
R_6 is unsubstituted or substituted C_1-C_{18}alkyl or aryl; cyano; halogen; nitro; -$COOR_{12}$ or -SO_3R_{12} wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; -SR_{13}, -SO_2R_{13} or -OR_{13} wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; -$NR_{14}R_{15}$, -(C_1-C_6alkylene)-$NR_{14}R_{15}$, -$N^{\oplus}R_{14}R_{15}R_{16}$, -($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$NR_{14}R_{15}$, -$N[(C_1$-$C_6$alkylene)-$NR_{14}R_{15}]_2$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N[(C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$, -$N(R_{13})$-N-$R_{14}R_{15}$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$, wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, and

R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11}, each independently of the others, is as defined above for R_6 or is hydrogen or unsubstituted or substituted aryl,

with the proviso that

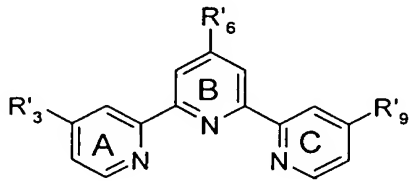
(i) at least one of the substituents $R_1 - R_{11}$ contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn, $R_1 - R_5$ and $R_7 - R_{11}$ are hydrogen and R_6 is



In this context the definitions and preferred meanings indicated above for the compounds of formula (1) apply to the metal complex compounds of formula (1a).

The ligand L of the metal complex compounds of formula (1a) is especially a compound of formula (3)



(3),

wherein

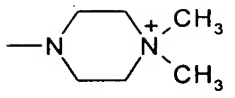
R'_6 is C_1-C_{12}alkyl; phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy; cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N[(C_1$-C_6alkylene$)$-$NR_{14}R_{15}]_2$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N[(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}]_2$, $-N(R_{13})$-N-$R_{14}R_{15}$ or $-N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, piperazine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised, and

R'_3 and R'_9 are as defined above or are hydrogen,

with the proviso that

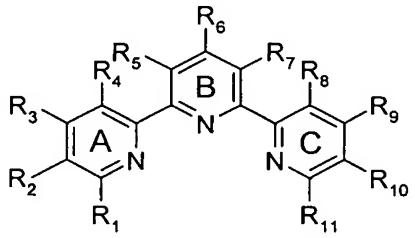
(i) at least one of the substituents R'_3, R'_6 and R'_9 is a radical $-(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N[(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}]_2$ or $-N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; or $-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N[(C_1$-C_6alkylene$)$-$NR_{14}R_{15}]_2$ or $-N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised, and that

(iii) Y is neither I^- nor Cl^- if Me is Mn(II), R'_3 and R'_9 are hydrogen and R'_6 is



In this context the definitions and preferred meanings indicated above for R'_6 and R'_3 and R'_9 likewise apply.

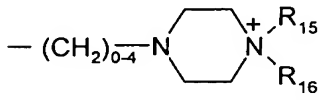
The present invention relates also to novel ligands of formula (2b)



(2b),

wherein

R_6 is cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(CH_2)_{1\text{-}6}NR_{14}R_{15}$, $-N(R_{13})-(CH_2)_{1\text{-}6}-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-N-R_{14}R_{15}$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, or unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised; or a radical



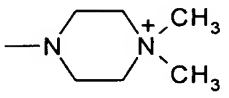
wherein R_{15} and R_{16} are as defined above and the ring may be unsubstituted or substituted, and

R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11}, each independently of the others, has a meaning indicated above for R_6 or is hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl,

with the proviso that

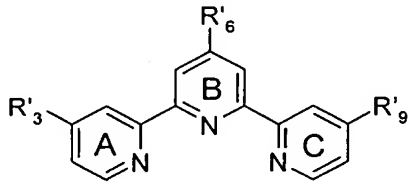
(i) at least one of the substituents $R_1 - R_{11}$ contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if R_1 - R_5 and R_7 - R_{11} are hydrogen and R_6 is



In this context the definitions and preferred meanings indicated above for the ligands of formula (2) apply.

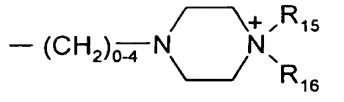
Preference is given to ligands of formula (3)



(3),

wherein

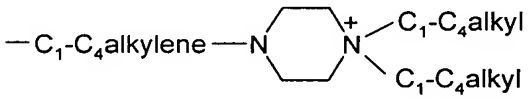
R'_6 is cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthyl-amino, phenyl, phenoxy or by naphthoxy, wherein the amino groups may or may not be quaternised; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(CH_2)_{1-6}-NR_{14}R_{15}$, $-N(R_{13})-(CH_2)_{1-6}-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-N-R_{14}R_{15}$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised; or a radical



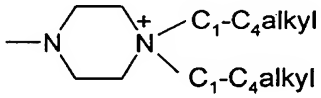
wherein R_{15} and R_{16} are as defined above, preferably C_1-C_4alkyl, and the ring may be unsubstituted or substituted, and

R'_3 and R'_9 are as defined above or are hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above. In this context, the definitions, provisos and preferred meanings indicated above for R'_6 and R'_3 and R'_9 for the ligands of the metal complex compounds of formula (3) likewise apply.

Especially preferred ligands of formula (3) are characterised in that R'_3, R'_6 and R'_9 are as defined above and at least one of the substituents R'_3, R'_6 and R'_9 is a radical

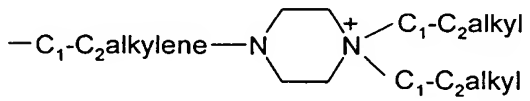


or



wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each of which independently of the other is unbranched or branched, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted.

Very especially preferred ligands of formula (3) are characterised in that R'_3, R'_6 and R'_9 are as defined above and at least one of the substituents R'_3, R'_6 and R'_9 is a radical



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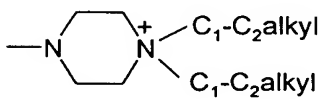
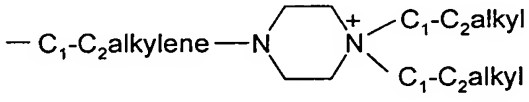


wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the unbranched alkyl groups, each independently of the other, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted.

Even more especially preferred ligands of formula (3) are characterised in that R'_3 and/or R'_9 is/are a radical



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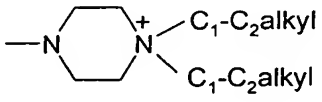


, and

R'_6 is OH.

The metal complex compounds of formula (1) are preferably used together with peroxy compounds. Examples that may be mentioned in that regard include the following uses:
a) the bleaching of spots or stains on textile material in the context of a washing process;
b) the prevention of redeposition of migrating dyes during the washing of textile material;
c) the cleaning of hard surfaces, especially wall tiles or floor tiles, for example for removing stains caused by the action of molds (mold stains);
d) use in washing and cleaning solutions having an antibacterial action;
e) as pretreatment agents for bleaching textiles;
f) as catalysts in selective oxidation reactions in the context of organic synthesis.

A further use relates to the use of the metal complex compounds of formula (1) as catalysts for reactions with peroxy compounds for bleaching in the context of paper-making. This relates especially to the bleaching of pulp, which can be carried out in accordance with customary processes. Also of interest is the use of the metal complex compounds of formula (1) as catalysts for reactions with peroxy compounds for the bleaching of waste printed paper.

Preference is given to the bleaching of spots or stains on textile material, the prevention of the redeposition of migrating dyes in the context of a washing process, or the cleaning of hard surfaces, especially wall tiles or floor tiles. In this case the preferred metals are manganese and/or iron.

It should be emphasised that the metal complex compounds do not cause any appreciable damage to fibres and dyeings, for example in the bleaching of textile material.

Processes for preventing the redeposition of migrating dyes in a washing liquor are usually carried out by adding to the washing liquor, which contains a peroxide-containing washing agent, one or more metal complex compounds of formula (1) in an amount of from 0.1 to 200 mg, preferably from 1 to 75 mg, especially from 3 to 50 mg, per litre of washing liquor. Alternatively, a washing agent can be added which already contains one or two metal complex compounds. It will be understood that in such an application, as well as in the other applications, the metal complex compounds of formula (1) can alternatively be formed *in situ*, the metal salt (e.g. manganese(II) salt, such as manganese(II) chloride, and/or iron(II) salt, such as iron(II) chloride) and the ligand being added in the desired molar ratios.

In addition, the present invention relates to a combined process for preventing the redeposition of migrating dyes and for simultaneous bleaching of spots or stains on textile material. For that purpose there are used mixtures of metal complexes of formula (1), especially mixtures of manganese complexes of formula (1) with iron complexes of formula (1). Special preference is given to mixtures of manganese complexes of formula (1) with iron complexes of formula (1'), which corresponds to formula (1) but does not contain any quaternised nitrogen atoms. Processes for preventing the redeposition of migrating dyes in a washing liquor are usually carried out by adding to the washing liquor, which contains a peroxide-containing washing agent, the mixture of quaternised manganese complexes of formula (1) and the non-quaternised iron complexes of formula (1') in an amount of from 0.1 to 200 mg, preferably from 1 to 75 mg, especially from 3 to 50 mg, per litre of washing liquor. Alternatively, a washing agent can be added which already contains the corresponding metal complex mixture. It will be understood that in such an application, as well as in the other applications, the metal complex compounds of formula (1) can alternatively be formed *in situ*, the metal salt (e.g. manganese(II) salt, such as manganese(II) chloride, and/or iron(II) salt, such as iron(II) chloride) and the ligand being added in the desired molar ratios.

The present invention relates to mixtures of manganese complexes of formula (I) with iron complexes of formula (I'). The compounds of formula (1') correspond to those of formula (1) but do not contain any quaternised nitrogen atoms.

The present invention relates also to a washing, cleaning, disinfecting or bleaching agent, containing

I) 0 - 50 %, preferably 0 - 30 %, A) of an anionic surfactant and/or B) of a non-ionic surfactant,

II) 0 - 70 %, preferably 0 - 50 %, C) of a builder substance,

III) 1 - 99 %, preferably 1 - 50 %, D) of a peroxide or a peroxide-forming substance, and

IV) E) metal complex compounds of formula (1) in an amount which, in the liquor, gives a concentration of 0.5 – 50 mg/litre of liquor, preferably 1 - 30 mg/litre of liquor, when from 0.5 to 20 g/litre of the washing, cleaning, disinfecting and bleaching agent are added to the liquor.

The above percentages are in each case percentages by weight, based on the total weight of the agent. The agents preferably contain from 0.005 to 2 % of a metal complex compound of formula (1), especially from 0.01 to 1 % and preferably from 0.05 to 1 %.
When the agents according to the invention comprise a component A) and/or B), the amount thereof is preferably 1 - 50 %, especially 1 - 30 %.

When the agents according to the invention comprise a component C), the amount thereof is preferably 1 - 70 %, especially 1 - 50 %. Special preference is given to an amount of from 5 to 50 % and especially an amount of from 10 to 50 %.

Corresponding washing, cleaning, disinfecting or bleaching processes are usually carried out by using an aqueous liquor comprising a peroxide and from 0.1 to 200 mg of one or more compounds of formula (1) per litre of liquor. The liquor preferably contains from 1 to 30 mg of the compound of formula (1) per litre of liquor.

The agent according to the invention can be, for example, a peroxide-containing complete washing agent or a separate bleaching additive. A bleaching additive is used for removing coloured stains on textiles in a separate liquor before the clothes are washed with a bleach-

free washing agent. A bleaching additive can also be used in a liquor together with a bleach-free washing agent.

The washing or cleaning agent according to the invention can be in solid or liquid form, for example in the form of a liquid, non-aqueous washing agent, comprising not more than 5 % by weight water, preferably comprising from 0 to 1 % by weight water, and, as base, a suspension of a builder substance in a non-ionic surfactant, for example as described in GB-A-2 158 454.

The washing or cleaning agent is preferably in the form of a powder, tablet (single- or multi-layered) or, especially, granules.

The latter can be prepared, for example, by first preparing an initial powder by spray-drying an aqueous suspension containing all the components listed above except for components D) and E), and then adding the dry components D) and E) and mixing everything together. It is also possible to add component E) to an aqueous suspension containing components A), B) and C), then to carry out spray-drying and then to mix component D) with the dry mass.

It is also possible to start with an aqueous suspension that contains components A) and C), but none or only some of component B). The suspension is spray-dried, then component E) is mixed with component B) and added, and then component D) is mixed in in the dry state.

It is also possible to mix all the components together in the dry state.

The anionic surfactant A) may be, for example, a sulfate, sulfonate or carboxylate surfactant or a mixture thereof. Preferred sulfates are those having from 12 to 22 carbon atoms in the alkyl radical, optionally in combination with alkyl ethoxysulfates in which the alkyl radical has from 10 to 20 carbon atoms.

Preferred sulfonates are, for example, alkylbenzenesulfonates having from 9 to 15 carbon atoms in the alkyl radical. The cation in the case of anionic surfactants is preferably an alkali metal cation, especially sodium.

Preferred carboxylates are alkali metal sarcosinates of formula R_{19}-CO-N(R_{20})-$CH_2COOM'^1$ wherein R_{19} is alkyl or alkenyl having from 8 to 18 carbon atoms in the alkyl or alkenyl radical, R_{20} is C_1-C_4alkyl and M'^1 is an alkali metal.
The non-ionic surfactant B) can be, for example, a condensation product of from 3 to 8 mol of ethylene oxide with 1 mol of a primary alcohol having from 9 to 15 carbon atoms.

As builder substance C) there come into consideration, for example, alkali metal phosphates, especially tripolyphosphates, carbonates or hydrogen carbonates, especially their sodium salts, silicates, aluminosilicates, polycarboxylates, polycarboxylic acids, organic phosphonates, aminoalkylenepoly(alkylenephosphonates) or mixtures of those compounds.

Especially suitable silicates are sodium salts of crystalline layered silicates of the formula $NaHSi_tO_{2t+1}.pH_2O$ or $Na_2Si_tO_{2t+1}.pH_2O$ wherein t is a number from 1.9 to 4 and p is a number from 0 to 20.

Among the aluminosilicates, preference is given to those commercially available under the names zeolite A, B, X and HS, and also to mixtures comprising two or more of those components.

Among the polycarboxylates, preference is given to polyhydroxycarboxylates, especially citrates, and acrylates and also copolymers thereof with maleic anhydride. Preferred polycarboxylic acids are nitrilotriacetic acid, ethylenediaminetetraacetic acid and ethylenediamine disuccinate either in racemic form or in the enantiomerically pure (S,S) form.

Phosphonates or aminoalkylenepoly(alkylenephosphonates) that are especially suitable are alkali metal salts of 1-hydroxyethane-1,1-diphosphonic acid, nitrilotris(methylene-phosphonic acid), ethylenediaminetetramethylenephosphonic acid and diethylenetriamine-pentamethylenephosphonic acid.

As the peroxide component D) there come into consideration, for example, the organic and inorganic peroxides known in the literature and available commercially

that bleach textile materials at conventional washing temperatures, for example at from 10 to 95°C.

The organic peroxides are, for example, mono- or poly-peroxides, especially organic peracids or salts thereof, such as phthalimidoperoxycaproic acid, peroxybenzoic acid, diperoxydodecanedioic acid, diperoxynonanedioic acid, diperoxydecanedioic acid, diperoxyphthalic acid or salts thereof.

Preferably, however, inorganic peroxides are used such as, for example, persulfates, perborates, percarbonates and/or persilicates. It will be understood that mixtures of inorganic and/or organic peroxides can also be used. The peroxides may be in a variety of crystalline forms and have different water contents, and they may also be used together with other inorganic or organic compounds in order to improve their storage stability.

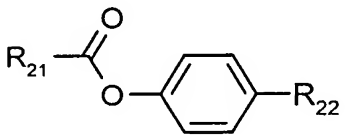
The peroxides are added to the agent preferably by mixing the components, for example using a screw metering system and/or a fluidised bed mixer.

The agents may comprise, in addition to the combination according to the invention, one or more optical brighteners, for example from the class bis-triazinylamino-stilbenedisulfonic acid, bis-triazolyl-stilbenedisulfonic acid, bis-styryl-biphenyl or bis-benzofuranylbiphenyl, a bis-benzoxalyl derivative, bis-benzimidazolyl derivative or coumarin derivative or a pyrazoline derivative.

The agent may also comprise suspending agents for dirt, for example sodium carboxymethylcellulose, pH regulators, for example alkali metal or alkaline earth metal silicates, foam regulators, for example soap, salts for regulating the spray-drying and the granulating properties, for example sodium sulfate, perfumes and, optionally, antistatic agents and softeners, enzymes such as amylase, bleaches, pigments and/or toning agents. Such constituents must especially be stable towards the bleaching agent used.

In addition to the bleach catalyst according to formula (1) it is also possible to use further transition metal salts or complexes known as bleach-activating active ingredients and/or conventional bleach activators, that is to say compounds that, under perhydrolysis conditions, yield unsubstituted or substituted perbenzo- and/or peroxo-carboxylic acids

having from 1 to 10 carbon atoms, especially from 2 to 4 carbon atoms. Suitable bleach activators include the customary bleach activators, mentioned at the beginning, that carry O- and/or N-acyl groups having the indicated number of carbon atoms and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), acylated glycolurils, especially tetraacetylglycoluril (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU), acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), compounds of formula (6):



(6)

wherein R_{21} is a sulfonate group, a carboxylic acid group or a carboxylate group, and wherein R_{22} is linear or branched (C_7-C_{15})alkyl, especially activators known under the names SNOBS, SLOBS and DOBA, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran, and also acetylated sorbitol and mannitol and acylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetyllactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. It is also possible to use the combinations of conventional bleach activators known from German Patent Application DE-A-44 43 177. Nitrile compounds that form perimine acids with peroxides also come into consideration as bleach activators.

Further preferred additives to the agents according to the invention are polymers which, during the washing of textiles, prevent staining caused by dyes in the washing liquor that have been released from the textiles under the washing conditions. Such polymers are preferably polyvinylpyrrolidones or polyvinylpyridine-N-oxides which may have been modified by the incorporation of anionic or cationic substituents, especially those having a molecular weight in the range of from 5000 to 60 000, more especially from 10 000 to 50 000. Such polymers are preferably used in an amount of from 0.05 to 5 % by weight, especially from 0.2 to 1.7 % by weight, based on the total weight of the washing agent.

The invention relates also to granules that comprise the catalysts according to the invention and are suitable for incorporation into a powder- or granule-form washing, cleaning or bleaching agent. Such granules preferably comprise:

a) from 1 to 99 % by weight, preferably from 1 to 40 % by weight, especially from 1 to 30 % by weight, of a metal complex compound of formula (1), especially of formula (1a),
b) from 1 to 99 % by weight, preferably from 10 to 99 % by weight, especially from 20 to 80 % by weight, of a binder,
c) from 0 to 20 % by weight, especially from 1 to 20 % by weight, of an encapsulating material,
d) from 0 to 20 % by weight of a further additive and
e) from 0 to 20 % by weight of water.

As binder (b) there come into consideration anionic dispersants, non-ionic dispersants, polymers and waxes that are water-soluble, dispersible or emulsifiable in water.

The anionic dispersants used are, for example, commercially available water-soluble anionic dispersants for dyes, pigments etc..
The following products, especially, come into consideration: condensation products of aromatic sulfonic acids and formaldehyde, condensation products of aromatic sulfonic acids with unsubstituted or chlorinated diphenyls or diphenyl oxides and optionally formaldehyde, (mono-/di-)alkylnaphthalenesulfonates, sodium salts of polymerised organic sulfonic acids, sodium salts of polymerised alkylnaphthalenesulfonic acids, sodium salts of polymerised alkylbenzenesulfonic acids, alkylarylsulfonates, sodium salts of alkyl polyglycol ether sulfates, polyalkylated polynuclear arylsulfonates, methylene-linked condensation products of arylsulfonic acids and hydroxyarylsulfonic acids, sodium salts of dialkylsulfosuccinic acids, sodium salts of alkyl diglycol ether sulfates, sodium salts of polynaphthalenemethane-sulfonates, lignosulfonates or oxylignosulfonates or heterocyclic polysulfonic acids.

Especially suitable anionic dispersants are condensation products of naphthalenesulfonic acids with formaldehyde, sodium salts of polymerised organic sulfonic acids, (mono-/di-)-alkylnaphthalenesulfonates, polyalkylated polynuclear arylsulfonates, sodium salts of polymerised alkylbenzenesulfonic acids, lignosulfonates, oxylignosulfonates and condensation products of naphthalenesulfonic acid with a polychloromethyldiphenyl.

Suitable non-ionic dispersants are especially compounds having a melting point of, preferably, at least 35°C that are emulsifiable, dispersible or soluble in water, for example the following compounds:

1. fatty alcohols having from 8 to 22 carbon atoms, especially cetyl alcohol;
2. addition products of, preferably, from 2 to 80 mol of alkylene oxide, especially ethylene oxide, wherein some of the ethylene oxide units may have been replaced by substituted epoxides, such as styrene oxide and/or propylene oxide, with higher unsaturated or saturated monoalcohols, fatty acids, fatty amines or fatty amides having from 8 to 22 carbon atoms or with benzyl alcohols, phenyl phenols, benzyl phenols or alkyl phenols, the alkyl radicals of which have at least 4 carbon atoms;
3. alkylene oxide, especially propylene oxide, condensation products (block polymers);
4. ethylene oxide/propylene oxide adducts with diamines, especially ethylenediamine;
5. reaction products of a fatty acid having from 8 to 22 carbon atoms and a primary or secondary amine having at least one hydroxy-lower alkyl or lower alkoxy-lower alkyl group, or alkylene oxide addition products of such hydroxyalkyl-group-containing reaction products;
6. sorbitan esters, preferably with long-chain ester groups, or ethoxylated sorbitan esters, such as polyoxyethylene sorbitan monolaurate having from 4 to 10 ethylene oxide units or polyoxyethylene sorbitan trioleate having from 4 to 20 ethylene oxide units;
7. addition products of propylene oxide with a tri- to hexa-hydric aliphatic alcohol having from 3 to 6 carbon atoms, for example glycerol or pentaerythritol; and
8. fatty alcohol polyglycol mixed ethers, especially addition products of from 3 to 30 mol of ethylene oxide and from 3 to 30 mol of propylene oxide with aliphatic monoalcohols having from 8 to 22 carbon atoms.

Especially suitable non-ionic dispersants are surfactants of formula

$$R_{23}\text{-O-(alkylene-O)}_n\text{-}R_{24} \qquad (7),$$

wherein

R_{23} is C_8-C_{22}alkyl or C_8-C_{18}alkenyl;

R_{24} is hydrogen; C_1-C_4alkyl; a cycloaliphatic radical having at least 6 carbon atoms; or benzyl;

"alkylene" is an alkylene radical having from 2 to 4 carbon atoms; and

n is a number from 1 to 60.

The substituents R_{23} and R_{24} in formula (7) are advantageously the hydrocarbon radical of an unsaturated or, preferably, saturated aliphatic monoalcohol having from 8 to 22 carbon atoms. The hydrocarbon radical may be straight-chain or branched. Preferably, R_{23} and R_{24} are each independently of the other an alkyl radical having from 9 to 14 carbon atoms.

Aliphatic saturated monoalcohols that come into consideration include natural alcohols such as, for example, lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, and also synthetic alcohols such as, for example, 2-ethylhexanol, 1,1,3,3-tetramethylbutanol, octan-2-ol, isononyl alcohol, trimethylhexanol, trimethylnonyl alcohol, decanol, C_9-C_{11}oxo-alcohol, tridecyl alcohol, isotridecyl alcohol and linear primary alcohols (Alfols) having from 8 to 22 carbon atoms. Some examples of such Alfols are Alfol (8-10), Alfol (9-11), Alfol (10-14), Alfol (12-13) and Alfol (16-18). ("Alfol" is a registered trade mark.)

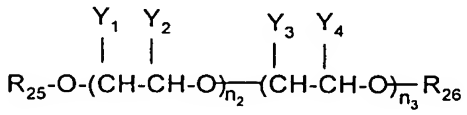
Unsaturated aliphatic monoalcohols are, for example, dodecenyl alcohol, hexadecenyl alcohol and oleyl alcohol.

The alcohol radicals may be present singly or in the form of mixtures of two or more components such as, for example, mixtures of alkyl and/or alkenyl groups that are derived from soybean fatty acids, palm kernel fatty acids or tallow oils.

(Alkylene-O) chains are preferably divalent radicals of the formulae

$$-(CH_2\text{-}CH_2\text{-}O)-,\quad -(CH(CH_3)\text{-}CH_2\text{-}O)-\quad \text{or} \quad -(CH_2\text{-}CH(CH_3)\text{-}O)-$$

Examples of a cycloaliphatic radical are cycloheptyl, cyclooctyl and preferably cyclohexyl. As non-ionic dispersants there come into consideration especially surfactants of formula



(8)

wherein

R_{25} is C_8-C_{22}alkyl;

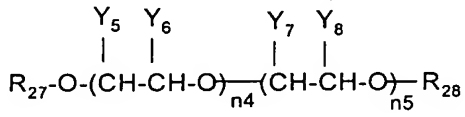
R_{26} is hydrogen or C_1-C_4alkyl;

Y_1, Y_2, Y_3 and Y_4 are each independently of the others hydrogen, methyl or ethyl;

n_2 is a number from 0 to 8; and

n_3 is a number from 2 to 40.

Further important non-ionic dispersants correspond to formula



(9),

wherein

R_{27} is C_9-C_{14}alkyl;

R_{28} is C_1-C_4alkyl;

Y_5, Y_6, Y_7 and Y_8 are each independently of the others hydrogen, methyl or ethyl, one of the radicals Y_5 and Y_6 and one of the radicals Y_7 and Y_8 always being hydrogen; and

n_4 and n_5 are each independently of the other an integer from 4 to 8.

The non-ionic dispersants of formulae (7) to (9) can be used in the form of mixtures. For example, as surfactant mixtures there come into consideration non-end-group-terminated fatty alcohol ethoxylates of formula (7), for example compounds of formula (7) wherein

R_{23} is C_8-C_{22}alkyl,

R_{24} is hydrogen, and

the alkylene-O chain is the radical -(CH_2-CH_2-O)-

and also end-group-terminated fatty alcohol ethoxylates of formula (9).

Examples of non-ionic dispersants of formulae (7), (8) and (9) include reaction products of a C_{10}-C_{13}fatty alcohol, for example a C_{13}oxo-alcohol, with from 3 to 10 mol of ethylene oxide, propylene oxide and/or butylene oxide or the reaction product of one mol of a C_{13}fatty alcohol with 6 mol of ethylene oxide and 1 mol of butylene oxide, it being possible for the addition products each to be end-group-terminated with C_1-C_4alkyl, preferably methyl or butyl.

Such dispersants can be used singly or in the form of mixtures of two or more dispersants.

Instead of, or in addition to, the anionic or non-ionic dispersant, the granules according to the invention may comprise a water-soluble organic polymer as binder. Such polymers may be used singly or in the form of mixtures of two or more polymers.

Water-soluble polymers that come into consideration are, for example, polyethylene glycols, copolymers of ethylene oxide with propylene oxide, gelatin, polyacrylates, polymethacrylates, polyvinylpyrrolidones, vinylpyrrolidones, vinyl acetates, polyvinylimidazoles, polyvinylpyridine-N-oxides, copolymers of vinylpyrrolidone with long-chain α-olefins, copolymers of vinylpyrrolidone with vinylimidazole, poly(vinylpyrrolidone/dimethylaminoethyl methacrylates), copolymers of vinylpyrrolidone/dimethylaminopropyl methacrylamides, copolymers of vinylpyrrolidone/dimethylaminopropyl acrylamides, quaternised copolymers of vinylpyrrolidones and dimethylaminoethyl methacrylates, terpolymers of vinylcaprolactam/vinylpyrrolidone/dimethylaminoethyl methacrylates, copolymers of vinylpyrrolidone and methacrylamidopropyl-trimethylammonium chloride, terpolymers of caprolactam/vinyl-pyrrolidone/dimethylaminoethyl methacrylates, copolymers of styrene and acrylic acid, polycarboxylic acids, polyacrylamides, carboxymethylcellulose, hydroxymethylcellulose, polyvinyl alcohols, polyvinyl acetate, hydrolysed polyvinyl acetate, copolymers of ethyl acrylate with methacrylate and methacrylic acid, copolymers of maleic acid with unsaturated hydrocarbons, and also mixed polymerisation products of the mentioned polymers.

Of those organic polymers, special preference is given to polyethylene glycols, carboxy-methylcellulose, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatin, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, and also polyacrylates, copolymers of ethyl acrylate with methacrylate and methacrylic acid, and polymethacrylates.

Suitable water-emulsifiable or water-dispersible binders also include paraffin waxes.

Encapsulating materials (c) include especially water-soluble and water-dispersible polymers and waxes. Of those materials, preference is given to polyethylene glycols, polyamides, polyacrylamides, polyvinyl alcohols, polyvinylpyrrolidones, gelatin, hydrolysed polyvinyl acetates, copolymers of vinylpyrrolidone and vinyl acetate, and also polyacrylates, paraffins, fatty acids, copolymers of ethyl acrylate with methacrylate and methacrylic acid, and polymethacrylates.

Further additives (d) include, for example, wetting agents, dust-removers, water-insoluble or water-soluble dyes or pigments, and also dissolution accelerators, optical brighteners and sequestering agents.

The preparation of the granules according to the invention is carried out, for example, starting from:
a) a solution or suspension with a subsequent drying/shaping step or
b) a suspension of the active ingredient in a melt with subsequent shaping and solidification.

a) First of all the anionic or non-ionic dispersant and/or the polymer and, if appropriate, the further additives are dissolved in water and stirred, if desired with heating, until a homogeneous solution has been obtained. The catalyst according to the invention is then dissolved or suspended in the resulting aqueous solution. The solids content of the solution should preferably be at least 30 % by weight, especially 40 to 50 % by weight, based on the total weight of the solution. The viscosity of the solution is preferably less than 200 mPas.

The aqueous solution so prepared, comprising the catalyst according to the invention, is then subjected to a drying step in which all water, with the exception of a residual amount, is removed, solid particles (granules) being formed at the same time. Known methods are suitable for producing the granules from the aqueous solution. In principle, both continuous methods and discontinuous methods are suitable. Continuous methods are preferred, especially spray-drying and fluidised bed granulation processes.

Especially suitable are spray-drying processes in which the active ingredient solution is sprayed into a chamber with circulating hot air. The atomisation of the solution is effected, for example, using unitary or binary nozzles or is brought about by the spinning effect of a rapidly rotating disc. In order to increase the particle size, the spray-drying process may be combined with an additional agglomeration of the liquid particles with solid nuclei in a fluidised bed that forms an integral part of the chamber (so-called fluid spray). The fine particles (<100 µm) obtained by a conventional spray-drying process may, if necessary after being separated from the exhaust gas flow, be fed as nuclei, without further treatment, directly into the atomizing cone of the atomiser of the spray-dryer for the purpose of agglomeration with the liquid droplets of the active ingredient.

During the granulation step, the water can rapidly be removed from the solutions comprising the catalyst according to the invention, binder and further additives. It is expressly intended that agglomeration of the droplets forming in the atomising cone, or the agglomeration of droplets with solid particles, will take place.

If necessary, the granules formed in the spray-dryer are removed in a continuous process, for example by a sieving operation. The fines and the oversize particles are either recycled directly to the process (without being redissolved) or are dissolved in the liquid active ingredient formulation and subsequently granulated again.

A further preparation method according to a) is a process in which the polymer is mixed with water and then the catalyst is dissolved/suspended in the polymer solution, thus forming an aqueous phase, the catalyst according to the invention being homogeneously distributed in that phase. At the same time or subsequently, the aqueous phase is dispersed in a water-immiscible liquid in the presence of a dispersion stabiliser in order that a stable dispersion is formed. The water is then removed from the dispersion by distillation, forming substantially dry particles. In those particles, the catalyst is homogeneously distributed in the polymer matrix.

The granules according to the invention are abrasion-resistant, low in dust, pourable and readily meterable. They can be added directly to a formulation, such as a washing agent formulation, in the desired concentration of the catalyst according to the invention.

Where the coloured appearance of the granules in the washing agent is to be suppressed, this can be achieved, for example, by embedding the granules in a droplet of a whitish meltable substance ("water-soluble wax") or by adding a white pigment (for example, TiO_2) to the granule formulation or, preferably, by encapsulating the granules in a melt consisting, for example, of a water-soluble wax, as described in EP-A-0 323 407, a white solid being added to the melt in order to reinforce the masking effect of the capsule.

b) The catalyst according to the invention is dried in a separate step prior to the melt-granulation and, if necessary, dry-ground in a mill so that all the solids particles are < 50 µm

in size. The drying is carried out in an apparatus customary for the purpose, for example in a paddle dryer, vacuum cabinet or freeze-dryer.

The finely particulate catalyst is suspended in the molten carrier material and homogenised. The desired granules are produced from the suspension in a shaping step with simultaneous solidification of the melt. The choice of a suitable melt-granulation process is made in accordance with the desired size of granules. In principle, any process which can be used to produce granules in a particle size of from 0.1 to 4 mm is suitable. Such processes are droplet processes (with solidification on a cooling belt or during free fall in cold air), melt-prilling (cooling medium gas/liquid), and flake formation with a subsequent comminution step, the granulation apparatus being operated continuously or discontinuously.

Where the coloured appearance of the granules prepared from a melt is to be suppressed in the washing agent, in addition to the catalyst it is also possible to suspend in the melt white or coloured pigments which, after solidification, impart the desired coloured appearance to the granules (for example, titanium dioxide).

If desired, the granules can be covered or encapsulated in an encapsulating material. Methods suitable for such an encapsulation include the customary methods and also the encapsulation of the granules by a melt consisting of, for example, a water-soluble wax, as described, for example, in EP-A-0 323 407, coacervation, complex coacervation and surface polymerisation.

Encapsulating materials (c) include, for example, water-soluble, water-dispersible or water-emulsifiable polymers and waxes.

Further additives (d) include e.g. wetting agents, dust-removers, water-insoluble or water-soluble dyes or pigments, and also dissolution accelerators, optical brighteners and sequestering agents.

Surprisingly, the metal complex compounds of formula (1) also have a markedly improved bleach-catalysing action on coloured stains on, for example, wall tiles or floor tiles.

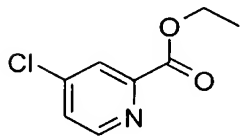
The use of metal complex compounds of formula (1) as catalysts for reactions with peroxy compounds in cleaning solutions for hard surfaces, especially for wall tiles or floor tiles, is therefore of special interest.

The metal complex compounds of formula (1) also have, together with peroxy compounds, outstanding antibacterial action. The use of the metal complex compounds of formula (1) for killing bacteria or for protecting against bacterial attack is therefore likewise of interest.

The metal complex compounds of formula (1) are also outstandingly suitable for selective oxidation in the context of organic synthesis, especially the oxidation of organic molecules, e.g. of olefins to form epoxides. Such selective transformation reactions are required especially in process chemistry. The invention accordingly relates also to the use of the metal complex compounds of formula (1) in selective oxidation reactions in the context of organic synthesis.

The following Examples serve to illustrate the invention but do not limit the invention thereto. Parts and percentages relate to weight, unless otherwise indicated. Temperatures are, unless otherwise stated, indicated in degrees Celsius.

Example 1: 4-Chloro-pyridine-2-carboxylic acid ethyl ester



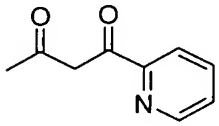
a) Step 1:
10.0 ml (0.130 mol) of N,N-dimethylformamide are added dropwise to 295 ml (4.06 mol) of thionyl chloride with stirring at 40°C. Then, over half an hour, 100 g (0.812 mol) of picolinic acid are added. The mixture is heated with caution to 70°C and is stirred at that temperature for 24 hours, the gases produced being taken off by way of a washing bottle containing sodium hydroxide solution. Concentration, further coevaporation three times using 100 ml of toluene each time and dilution with that solvent to 440 ml are carried out, and the solution is introduced into a mixture of 120 ml of absolute ethanol and 120 ml of toluene. The mixture is concentrated to about half its volume, cooled to 4°C, filtered under suction and washed with

toluene. 4-Chloro-pyridine-2-carboxylic acid ethyl ester hydrochloride is obtained in the form of a beige hygroscopic powder.

b) Step 2:

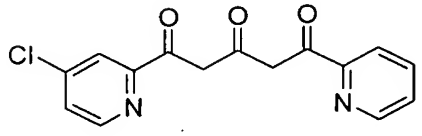
The hydrochloride obtained in Step 1 is taken up in 300 ml of ethyl acetate and 200 ml of deionised water and neutralised using 4N sodium hydroxide solution. After separation of the phases, extraction is carried out twice using 200 ml of ethyl acetate each time. The organic phases are combined, dried over sodium sulfate, filtered and concentrated. 4-Chloro-pyridine-2-carboxylic acid ethyl ester in the form of a brown oil which can, if required, be purified by distillation. ^{1}H NMR (360 MHz, $CDCl_3$): 8.56 (d, 1H, J=5.0 Hz); 8.03 (d, 1H, J=1.8 Hz); 7.39 (dd, 1H, J=5.4,1.8 Hz); 4.39 (q, 2H, J=7.0 Hz); 1.35 (t, 3 H, J=7.0 Hz).

Example 2: 1-Pyridin-2-yl-butane-1,3-dione



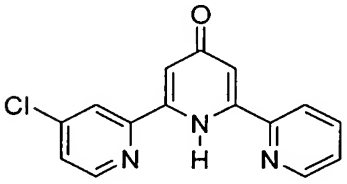
A solution of 8.71 g (150 mmol) of dry acetone in 100 ml of absolute tetrahydrofuran is added, under argon, to a solution of 20.42 g (300 mmol) of sodium ethanolate in 300 ml of absolute tetrahydrofuran. Then a solution of 22.68 g (150 mmol) of pyridine-2-carboxylic acid ethyl ester in 100 ml of absolute tetrahydrofuran is added dropwise over 20 minutes. The mixture is stirred for 15 hours at room temperature and for four hours at boiling point. Concentration is carried out using a rotary evaporator, 150 ml of water are added and neutralisation is carried out using glacial acetic acid. Extraction with diethyl ether is carried out twice; the organic extracts are combined and dried (sodium sulfate) and, after concentrating using a rotary evaporator, 1-pyridin-2-yl-butane-1,3-dione is obtained in the form of an orange oil. ^{1}H NMR (360 MHz, $CDCl_3$) for the enol tautomer: 15.8-15.5 (br s, OH); 8.60-8.55 (dm, 1H); 8.20-7.95 (dm, 1H); 7.79-7.71 (tm, 1H); 7.35-7.29 (m, 1H); 6.74 (s, 1H); 2.15 (s, 3H). Keto tautomer: CH_2 group at 4.20 ppm (ratio of enol to keto form = 87:13).

Example 3: 1-(4-Chloro-pyridin-2-yl)-5-pyridin-2-yl-pentane-1,3,5-trione



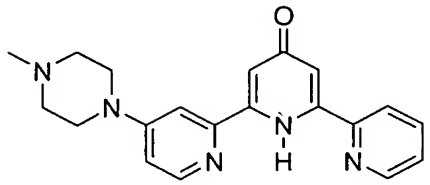
A mixture of 21.3 g (131 mmol) of 1-pyridin-2-yl-butane-1,3-dione and 36.3 g (196 mmol) of 4-chloro-pyridine-2-carboxylic acid ethyl ester in 100 ml of absolute tetrahydrofuran is added dropwise, at boiling point, over two hours, to 10.43 g (261 mmol, approx. 60 % dispersion) of sodium hydride in 200 ml of absolute tetrahydrofuran. Stirring is subsequently carried out for two hours more at 70°C, concentration is carried out using a rotary evaporator and then 200 ml of water are added at 4°C with caution. Neutralisation is carried out using 5N hydrochloric acid, and 1-(4-chloro-pyridin-2-yl)-5-pyridin-2-yl-pentane-1,3,5-trione is filtered off in the form of a yellow-green solid. The dried, poorly soluble product is used in further processing without taking special purification steps.

Example 4: 4-Chloro-1'H-[2,2';6',2'']terpyridin-4'-one



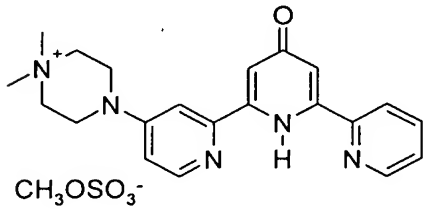
110 ml of 25 % ammonium hydroxide solution are added to 1-(4-chloro-pyridin-2-yl)-5-pyridin-2-yl-pentane-1,3,5-trione, obtained as described hereinabove, in 100 ml of isopropanol and refluxing is carried out for 4.5 hours. At room temperature, adjustment to pH = 5 using 6N hydrochloric acid and filtration are carried out. The residue is filtered over silica gel (eluant: chloroform/methanol/ammonium hydroxide solution 4:1:0.1) and concentrated. After recrystallising from acetone, 4-chloro-1'H-[2,2';6',2'']terpyridin-4'-one is obtained in the form of a grey solid which is used in further processing without taking special purification steps. ^{1}H NMR (360 MHz, DMSO-d_6): 8.72-8.63 (m, 2H); 8.62-8.53 (m, 2H); 7.98 (ddd, 1H, J=7.7,7.7,1.8 Hz); 7.87 (d, 1H, J=2.2 Hz); 7.83 (d, 1H, J=2.2 Hz); 7.59 (dd, 1H, J=5.4,2.2 Hz); 7.43-7.51 (m, 1H); 2.07 (s, 1H).

Example 5: 4-(4-Methyl-piperazin-1-yl)-1'H-[2,2';6',2"]terpyridin-4'-one (ligand L1)



A mixture of 5.22 g (18.4 mmol) of 4-chloro-1'H-[2,2';6',2"]terpyridin-4'-one, 18.36 g (184 mmol, 20.4 ml) of 1-methyl-piperazine and 125 mg (0.92 mmol, 0.05 equivalent) of zinc(II) chloride in 80 ml of 2-methyl-2-butanol is refluxed for 30 hours. Concentration to dryness is carried out using a rotary evaporator. 100 ml of water are added and neutralisation is carried out using concentrated hydrochloric acid. After extracting four times with chloroform and combining and drying (sodium sulfate) the organic extracts, the crude product is obtained, which is then recrystallised from acetonitrile. 4-(4-Methyl-piperazin-1-yl)-1'H-[2,2';6',2"]terpyridin-4'-one is obtained in the form of a white solid. ^{1}H NMR (360 MHz, $CDCl_3$): 8.69 (d, 1H, 4.5 Hz); 8.32 (d, 1H, J=5.9 Hz); 7.92-7.74 (m, 2H); 7.37-7.30 (m, 1H); 7.20 (d, 1H, J=2.3 Hz); 7.01 (s, 1H); 6.98 (s, 1H); 6.71-6.63 (m, 1H); 3.45-3.35 (tm, 4H); 2.58-2.48 (tm, 4H); 2.32 (s, 3H).

Example 6: 1,1-Dimethyl-4-(4'-oxo-1',4'-dihydro-[2,2';6',2"]terpyridin-4-yl)-piperazin-1-ium methosulfate (ligand L2)



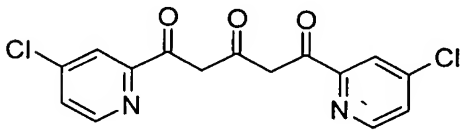
0.33 ml (3.5 mmol, 442 mg) of dimethyl sulfate is added dropwise to a suspension of 1.22 g (3.5 mmol) of 4-(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2"]terpyridin-4'-one in 60 ml of acetone. After 17 hours, the crude product is filtered off and washed (acetone and/or dichloromethane) and it is then recrystallised from methanol. 1,1-Dimethyl-4-(4'-oxo-1',4'-dihydro-[2,2';6',2"]terpyridin-4-yl)-piperazin-1-ium methosulfate is obtained in the form of a

white solid. $C_{22}H_{27}N_5O_5S$ *0.09 H_2O, 475.17; calculated C 55.61 H 5.77 N 14.74 S 6.75 H_2O 0.34; found C 55.56 H 5.85 N 14.63 S 6.75 H_2O 0.33. ^1H NMR (360 MHz, D_2O): 8.31 (d, 1H, J=4.1 Hz); 7.76 (dd, 1H, J=7.7); 7.64 (d, 1H, J=7.7 Hz); 7.58 (d, 1H, J=5.4 Hz); 7.22 (dd, 1H, J=7.2,5.0 Hz), 6.71 (s, 1H; 6.48 (dm, 1H); 6.46-6.39 (dm, 1H); 6.34 (dm, 1H); 3.67 (s, 3H); 3.48 (br s, 8 H); 3.19 (s, 6H).

Example 7: Manganese(II) complex with 1,1-dimethyl-4-(4'-oxo-1',4'-dihydro-[2,2';6',2'']terpyridin-4-yl)-piperazin-1-ium methosulfate

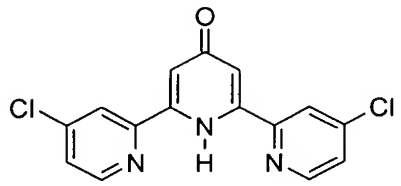
A solution of 37.6 mg (0.19 mmol) of manganese(II) chloride tetrahydrate in 4 ml of methanol is added to a suspension of 1,1-dimethyl-4-(4'-oxo-1',4'-dihydro-[2,2';6',2'']terpyridin-4-yl)-piperazin-1-ium methosulfate in 4 ml of methanol. Concentration is then carried out using a rotary evaporator (30°C, 20 mbar final pressure). The manganese complex of formula $C_{22}H_{27}Cl_2MnN_5O_5S$ *0.38 H_2O (FW = 606.24) is obtained in the form of a yellow powder; calculated C 43.59 H 4.62 N 11.55 S 5.29 Cl 11.70 Mn 9.06 H_2O 1.13; found C 43.54 H 4.50 N 11.73 S 5.07 Cl 11.69 Mn 9.06 H_2O 1.14.

Example 8: 1,5-Bis(4-chloro-pyridin-2-yl)-pentane-1,3,5-trione



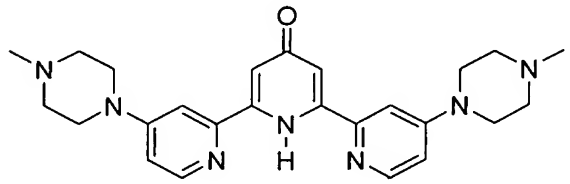
In a nitrogen atmosphere, 4 g (0.1 mol, approx. 60 % dispersion) of sodium hydride are initially introduced into 100 ml of absolute tetrahydrofuran. At < 56°C, over two hours, a solution of 18.5 g (0.1 mol) of 4-chloro-pyridine-2-carboxylic acid ethyl ester and 2.32 g (0.04 mol) of dried acetone in 75 ml of THF is added dropwise. The red suspension is then poured into 900 ml of water with caution. Neutralisation is carried out using 6N HCl, tetrahydrofuran is driven off using a rotary evaporator, and the yellow to beige 1,5-bis(4-chloro-pyridin-2-yl)-pentane-1,3,5-trione formed is filtered off. The dried, poorly soluble product is used in further processing without taking special purification steps. IR (cm^{-1}): 1619 (m); 1564 (s); 1546 (s); 1440 (m); 1374 (s); 1156 (m); 822 (w).

Example 9: 4,4''-Dichloro-1'H-[2,2';6',2'']terpyridin-4'-one



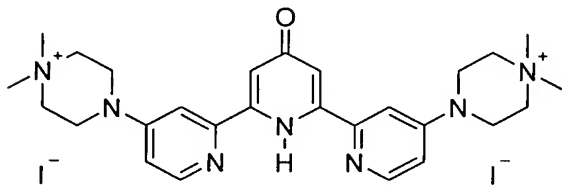
38.5 g (0.114 mol) of 1,5-bis(4-chloro-pyridin-2-yl)-pentane-1,3,5-trione are suspended in 1.25 litres of 2-propanol. At 60°C - 70°C, over five and a half hours, a total of 230 ml of 25 % (w/w) ammonia solution is added. Cooling to 4°C is carried out and the whitish 4,4''-dichloro-1'H-[2,2';6',2'']terpyridin-4'-one formed is filtered off. ^{1}H NMR (360 MHz, DMSO-d_6): 8.65 (d, 2H, J=5.4 Hz); 8.57 (d, 2H, J=2.2 Hz); 7.82 (s, 2H); 7.59 (dd, 2H, J=5.4,2.2 Hz).

Example 10: 4,4''-Bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one (ligand L3)



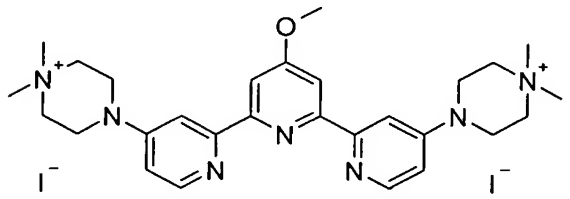
A mixture of 10.89 g (34.2 mmol) of 4,4''-dichloro-1'H-[2,2';6',2'']terpyridin-4'-one, 68.6 g (685 mmol, 76.1 ml) of 1-methyl-piperazine and 233 mg (1.71 mmol, 0.05 equivalent) of zinc(II) chloride in 200 ml of 2-methyl-2-butanol is refluxed for 24 hours. Concentration to dryness is carried out using a rotary evaporator. The crude product is recrystallised from ethyl acetate/methanol 33:1 (v/v) and taken up in 100 ml of water. Adjustment to pH = 8-9 using 4N sodium hydroxide solution is carried out and slightly beige 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one is filtered off. ^{1}H NMR (360 MHz, $CDCl_3$): 8.32 (d, 2H, J=5.9 Hz); 7.18 (dm, 2H); 6.93 (s, 2H); 6.66 (dd, 2H; J=5.9,2.3 Hz); 3.41-3.32 (tm, 8H); 2.55-2.44 (tm, 8H); 2.29 (s, 6H).

Example 11: Double quaternisation of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one using methyl iodide (ligand L4)



8.7 ml (19.9 g, 140 mmol) of methyl iodide are added dropwise to a suspension of 3.12 g (7 mmol) of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H- [2,2';6',2'']terpyridin-4'-one in 150 ml of acetonitrile. Stirring for five hours at room temperature and filtration are carried out and the resulting doubly quaternised, whitish 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one ($C_{27}H_{37}I_2N_7O$) is washed (acetonitrile). ^{1}H NMR (360 MHz, D_2O): 7.73 (d, 2H, J=5.9 Hz); 6.88 (s, 2H); 6.63-6.54 (dm, 2H); 6.45 (s, 2H); 3.69-3.43 (dm, 16H); 3.20 (s, 12H).

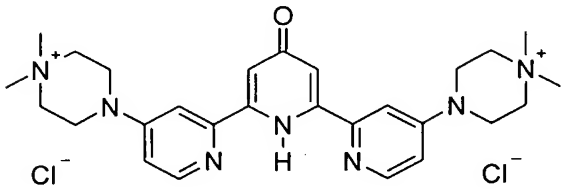
Example 11a: Tri-methylation of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one using methyl iodide (ligand L4a)



156 mg (0.35 mmol) of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one are added at 4°C to a suspension of a total of about 30 mg of sodium hydride (about 0.75 mmol, 60 % in mineral oil) in 3 ml of absolute N,N-dimethylformamide. Stirring is carried out for a further 20 minutes at that temperature, followed by warming to room temperature for one hour and cooling again. Then 66 µl (1.05 mmol) of methyl iodide are added dropwise and the mixture is stirred for 20 minutes in the cold state and thirty minutes at room temperature. After cooling again and adding 2 ml of water, white, tri-methylated 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one of formula $C_{28}H_{39}I_2N_7O$ is filtered off. ^{13}C NMR

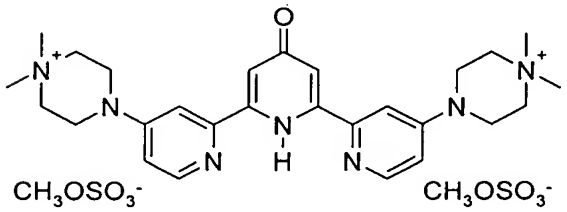
(40 MHz, DMSO-d_6): 167.2; 156.8; 155.6; 154.7; 149.8; 109.4; 106.4; 105.6; 59.9; 55.5; 50.4; 40.0.

Example 12: Anion exchange in the case of L4 (ligand L5)



0.96 g (1.32 mmol) of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one doubly quaternised using methyl iodide is dissolved in 10 ml of dilute HCl (pH=6). The solution is eluted over an ion exchange column (100 g DOWEX 1x8, 200-400 mesh, chloride form) and concentrated using a rotary evaporator. $C_{27}H_{37}Cl_2N_7O$*1.8 HCl*2 H_2O, calculated C 50.03 H 6.66 N 15.13 Cl 20.78, found C 50.47 H 6.67 N 14.90 Cl 20.4 (I content <0.3). ^{1}H NMR (400 MHz, D_2O): 8.17 (dm, 2H, J=7Hz); 7.59 (s, 2H); 7.46 (s, 2H); 7.15 (dm, 2H, J=7Hz); 4.14 (br s, 8H); 3.71 (br s, 8H); 3.30 (s, 12H).

Example 13: Double quaternisation of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one using dimethyl sulfate (ligand L6)



2.66 ml (27.92 mmol) of dimethyl sulfate are added dropwise to a suspension of 6.22 g (13.96 mmol) of 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one in 250 ml of acetone. After twenty hours, doubly quaternised, whitish 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one is filtered off and washed (acetone). $C_{29}H_{43}N_7O_9S_2$ *0.39 H_2O, 704.86; calculated C 49.42 H 6.26 N 13.91 S 9.10 H_2O 1.00; found C 49.30 H 6.19 N 13.85 S 8.99 H_2O 1.00. ^{1}H NMR (360 MHz, D_2O): 8.08 (d, J=5.9 Hz, 2H); 7.18 (dm, 2H); 6.79 (dd, J=5.9,2.3 Hz); 6.74 (s, 2H); 3.77-3.68 (m, 8H); 3.65 (s, 6 H); 3.59-3.50 (m, 8H).

Example 14: Manganese(II) complex with doubly quaternised 4,4''-bis(4-methyl-piperazin-1-yl)-1'H-[2,2';6',2'']terpyridin-4'-one

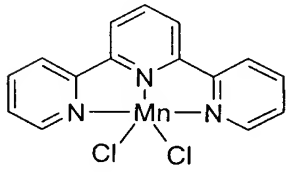
A solution of 119 mg (0.6 mmol) of manganese(II) chloride tetrahydrate in 11 ml of methanol is added to a suspension of 419 mg (0.6 mmol) of ligand $C_{29}H_{43}N_7O_9S_2$. Concentration is then carried out using a rotary evaporator (30°C, 20 mbar final pressure). The manganese complex of formula $C_{29}H_{43}Cl_2MnN_7O_9S_2$*2.22 H_2O (FW 863.67) is obtained in the form of a yellow powder; calculated C 40.33 H 5.54 N 11.35 S 7.43 Cl 8.21 Mn 6.36 H_2O 4.63; found C 41.10 H 5.35 N 11.77 S 7.18 Cl 8.36 Mn 5.91 H_2O 4.64.

APPLICATION EXAMPLES

Application Example 1: (Bleaching action in washing agents)

7.5 g of white cotton fabric and 2.5 g of tea-stained cotton fabric are treated in 80 ml of washing liquor. The liquor contains a standard washing agent (IEC 60456 A*) in a concentration of 7.5 g/l. The hydrogen peroxide concentration is 8.6 mmol/l. The catalyst concentration (1:1 complex of manganese(II) chloride tetrahydrate with the ligand in question, prepared in methanolic or aqueous solution) is 20 µmol/l. The washing process is carried out in a steel beaker in a LINITEST apparatus for 30 minutes at 40°C. For evaluating the bleaching results, the increase in the lightness DY (difference in lightness according to CIE) of the stains brought about by the treatment is determined spectrophotometrically in comparison with values obtained without the addition of catalyst.

The Mn complex of formula (10) mentioned in Table 1 hereinbelow for comparison purposes is the compound of formula



(10)

Table 1

Mn complex with ligand	DY increase
L1 (Example 5)	5.9
L2 (Example 6)	8.6
L3 (Example 10)	5.6
L4 (Example 11)	9.7
L5 (Example 12)	10.0
L6 (Example 13)	10.1
Terpyridine (10)	1.4

As can be seen from Table 1 above, the ligands having a quaternised nitrogen function in accordance with the invention exhibit far better bleaching action than the corresponding compounds on which they are based. All the complexes are greatly superior to the terpyridine reference system.

Application Example 2: (Catalytic bleaching of cellulose)
20 g of cellulose [TPP-CT CSF129, Ref. No. P-178635 (ISO 57.4)] are steeped in a litre of water for 65 hours and then stirred in a mixer for 2 minutes to give a paste-like pulp.
A bleaching bath containing 50 g of the pulp so prepared in 180 ml of water, 100µM of Dequest 2041 (sequestering agent), 8.6mM of hydrogen peroxide and 5µM of catalyst from Example 14 is maintained at 40°C for 30 minutes. At the same time 1N sodium hydroxide solution is metered-in in such a manner that a pH of 10.0 is maintained. Filtration and air-drying are then carried out. A sample that has been compressed to form a circular sheet of 10 cm diameter is then tested for the lightness Y obtained (according to CIE, reflectance spectroscopy). The results are compiled in the Table 2 hereinbelow.

Table 2

Test sample	Lightness Y
Untreated	61.9
Catalytically bleached	62.9

Application Example 3: (Action as catalyst for DTI (dye transfer inhibition))
In accordance with this application, the redeposition of migrating dyes in washing liquors, especially, should be avoided.

7.5 g of white cotton fabric are treated in 80 ml of washing liquor. The liquor contains a standard washing agent (IEC 60456 A*) in a concentration of 7.5 g/l, 8.6 mmol/litre of hydrogen peroxide and a solution of the test dye Reactive Blue 238. The catalyst solution is prepared beforehand in methanol by mixing an aqueous solution of equimolar amounts of iron(III) chloride and ligand L6 from Example 13. As a result a catalyst concentration of 50 µmol/litre in the liquor is established. The washing process is carried out in a steel beaker in a LINITEST apparatus for 30 minutes at 40°C. For testing the activity of the catalysts, the DTI activity is determined. The DTI (Dye Transfer Inhibition) activity a is defined as the following percentage:

$$a = ([Y(E) - Y(A)] / [Y(W) - Y(A)]) * 100$$

where Y(W), Y(A) and Y(E) are the CIE lightness values of the white material, of the material treated without the addition of catalyst and of the material treated with the addition of catalyst (in that order). a = 100% corresponds to a perfect catalyst which totally prevents the staining of the white material. The reflection spectra of the samples were measured using a SPECTRAFLASH 2000 and converted into lightness values (D65/10) in accordance with a standard CIE procedure.

The testing method described above results in a value a = 71 %.

Application Example 4: The use of the catalysts according to the invention causes hardly any additional fading of the dyes in dyed cotton laundry. When used as described above in Application Example 4, after treating dyed fabric five times, virtually no dye damage is recorded compared to the catalyst-free system. The values given in Table 3 hereinbelow are relative percentage dye losses, determined on the basis of Kubelka-Munk values at the respective absorption maximum.

Table 3

Cotton dyeing with dye	Dye loss (%) in system	
	with $MnCl_2$-L4 (50µM)	without catalyst
V Br 1	1	2
V Bl 4	7	4
R Br 17	13	15
D Bl 85	19	14

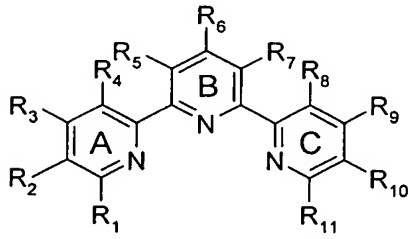
Application Example 5: (catalytic action for the epoxidation of olefins)
35 mg (0.05 mmol) of ligand L6 (Example 13), 10 mg (0.04 mmol) of manganese(II) acetate tetrahydrate and 0.32 mmol of sodium ascorbate are added to a solution of 1.09 ml (10 mmol) of ethyl acrylate in 0.5 ml of acetonitrile. The mixture is cooled in an ice bath and a 30 % hydrogen peroxide solution (2.27 g, 20 mmol) is added dropwise over 20 minutes. The mixture is then left for 16 hours at room temperature; it is diluted with diethyl ether and the phases are separated. The organic extract is dried over sodium sulfate, filtered and concentrated. The catalytic turnover number for the epoxide formed, ethyl oxirane-2-carboxylate, is determined by comparing the intensity of the epoxide methine proton at 3.38-3.42 ppm with an olefin signal of remaining starting material at 5.95 ppm as reference and is 39±5. Ethyl oxirane-2-carboxylate, epoxide signals ^{1}H NMR (360 MHz, $CDCl_3$): 2.68-2.89 (m, 2H, CH_2); 3.38-3.42 (m, 1H, CH). Without the addition of ligand, epoxide cannot be detected. (See also Berkessel, A. et al., *Tetrahedron Lett.* **1999**, *40*, 7965-7968).

Patent claims

1. Use of metal complex compounds of formula (1)

$$[L_nMe_mX_p]^zY_q \qquad (1),$$

wherein Me is manganese, titanium, iron, cobalt, nickel or copper,
X is a coordinating or bridging radical,
n and m are each independently of the other an integer having a value of from 1 to 8,
p is an integer having a value of from 0 to 32,
z is the charge of the metal complex,
Y is a counter-ion,
q = z/(charge Y), and
L is a ligand of formula (2)



(2),

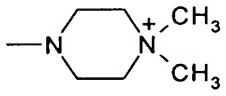
wherein
R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen; unsubstituted or substituted C_1-C_{18}alkyl or aryl; cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N[(C_1$-C_6alkylene$)$-$NR_{14}R_{15}]_2$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N[(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}]_2$, $-N(R_{13})$-N-$R_{14}R_{15}$ or $-N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking

them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms,

with the proviso that

(i) at least one of the substituents $R_1 - R_{11}$ contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn(II), $R_1 - R_5$ and $R_7 - R_{11}$ are hydrogen and R_6 is



as catalysts for oxidation reactions.

2. Use according to claim 1, characterised in that Me is manganese which is present in oxidation state II, III, IV or V.

3. Use according to claim 1, characterised in that Me is iron which is present in oxidation state II, III or IV.

4. Use according to one of claims 1, 2 and 3, characterised in that X is CH_3CN, H_2O, F^-, Cl^-, Br^-, HOO^-, O_2^{2-}, O^{2-}, $R_{17}COO^-$, $R_{17}O^-$, $LMeO^-$ or $LMeOO^-$, wherein R_{17} is hydrogen, $-SO_3C_1$-C_4alkyl or unsubstituted or substituted C_1-C_{18}alkyl or aryl, and L and Me are as defined in claim 1.

5. Use according to one of claims 1 to 4, characterised in that Y is $R_{17}COO^-$, ClO_4^-, BF_4^-, PF_6^-, $R_{17}SO_3^-$, $R_{17}SO_4^-$, SO_4^{2-}, NO_3^-, F^-, Cl^-, Br^-, I^-, citrate, tartrate or oxalate, wherein R_{17} is hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl.

6. Use according to one of claims 1 to 5, characterised in that n is an integer having a value of from 1 to 4, especially 1 or 2.

7. Use according to one of claims 1 to 6, characterised in that m is an integer having a value of 1 or 2, especially 1.

8. Use according to one of claims 1 to 7, characterised in that p is an integer having a value of from 0 to 4, especially 2.

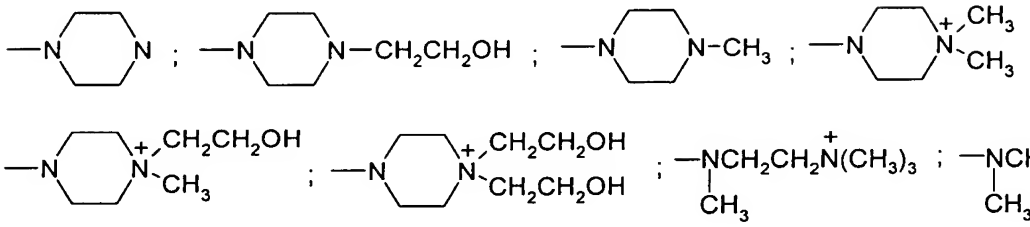
9. Use according to one of claims 1 to 8, characterised in that z is an integer having a value of from 8- to 8+.

10. Use according to one of claims 1 to 9, characterised in that aryl is phenyl or naphthyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy.

11. Use according to one of claims 1 to 10, characterised in that the 5-, 6- or 7-membered ring formed by R_{14} and R_{15} together with the nitrogen atom linking them is an unsubstituted or C_1-C_4alkyl-substituted pyrrolidine, piperidine, piperazine, morpholine or azepane ring, in which the nitrogen atoms may or may not be quaternised.

12. Use according to one of claims 1 to 11, characterised in that R_6 is C_1-C_{12}alkyl; phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy; cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$NR_{14}R_{15}$, $-N(R_{13})$-$(C_1$-C_6alkylene$)$-$N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})$-N-$R_{14}R_{15}$ or $-N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, piperazine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised and R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11} are as defined in claim 1 or are hydrogen.

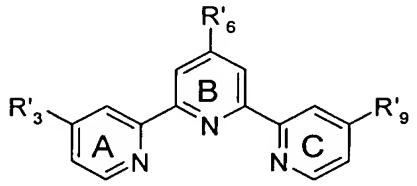
13. Use according to claim 12, characterised in that R_6 is



and

R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11} are as defined above or are hydrogen.

14. Use according to claim 12 or 13, characterised in that the ligand L is a compound of formula



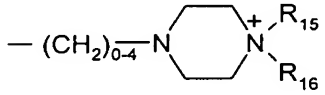
(3),

wherein

R'_3, R'_6 and R'_9 are as defined for R_6 in claim 12 or 13, it being possible in addition for R'_3 and R'_9 to be hydrogen.

15. Use according to claim 14, characterised in that R'_3, R'_6 and R'_9 are, each independently of the others, phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, phenyl or by hydroxyl; cyano; nitro; -$COOR_{12}$ or -SO_3R_{12} wherein R_{12} is in each case hydrogen, a cation, C_1-C_4alkyl or phenyl; -SR_{13}, -SO_2R_{13} or -OR_{13} wherein R_{13} is in each case hydrogen, C_1-C_4alkyl or phenyl; -$N(CH_3)$-NH_2 or -NH-NH_2; amino; N-mono- or N,N-di-C_1-C_4alkylamino unsubstituted or substituted by hydroxy in the alkyl moiety, wherein the nitrogen atoms, especially the nitrogen atoms not bonded to any of the three pyridine rings A, B or C, may or may not be quaternised; N-mono- or N,N-di-C_1-C_4alkyl-$N^{\oplus}R_{14}R_{15}R_{16}$ unsubstituted or substituted by hydroxy in the alkyl moiety, wherein R_{14}, R_{15} and R_{16} are each independently of the others hydrogen,

unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by at least one C_1-C_4alkyl radical or by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised; or N-mono- or N,N-di-C_1-C_4alkyl-$NR_{14}R_{15}$ unsubstituted or substituted by hydroxy in the alkyl moiety, R_{14} and R_{15} therein being as defined above; or a radical



wherein R_{15} and R_{16} are as defined above, preferably C_1-C_4alkyl, and the ring is unsubstituted or substituted, it likewise being possible for R'_3 and R'_9 also to be hydrogen.

16. Use according to claim 14 or 15, characterised in that R_6 is hydroxy.

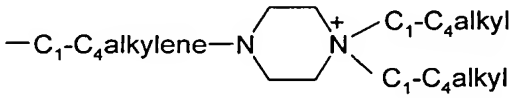
17. Use according to claims 1 to 13, characterised in that at least one of the substituents R_1 - R_{11}, preferably at least one of the substituents R_3, R_6 and/or R_9, is one of the following radicals
-(C_1-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$,
-$N[(C_1$-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is in each case hydrogen, C_1-C_4alkyl or phenyl and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; or
-$NR_{14}R_{15}$, -(C_1-C_6alkylene)-$NR_{14}R_{15}$, -$N(R_{13})$-(C_1-C_6alkylene)-$NR_{14}R_{15}$,
-$N[(C_1$-C_6alkylene)-$NR_{14}R_{15}]_2$ or -$N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

18. Use according to claims 14 to 16, characterised in that at least one of the substituents R_3, R'_6 and R'_9 , preferably R'_3 and/or R'_9, is one of the following radicals
-(C_1-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$,
-$N[(C_1$-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is in each case hydrogen, C_1-C_4alkyl or phenyl and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; or
-$NR_{14}R_{15}$, -(C_1-C_6alkylene)-$NR_{14}R_{15}$, -$N(R_{13})$-(C_1-C_6alkylene)-$NR_{14}R_{15}$,
-$N[(C_1$-C_6alkylene)-$NR_{14}R_{15}]_2$ or -$N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

19. Use according to claims 1 to 13, characterised in that at least one of the substituents R_1 – R_{11}, preferably at least one of the substituents R_3, R_6 and/or R_9, is one of the following radicals
-(C_1-C_4alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_4$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$,
-$N[(C_1$-C_6alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{12}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms; or
-$NR_{14}R_{15}$, -(C_1-C_6alkylene)-$NR_{14}R_{15}$, -$N(R_{13})$-(C_1-C_4alkylene)-$NR_{14}R_{15}$,
-$N[(C_1$-C_6alkylene)-$NR_{14}R_{15}]_2$ or -$N(R_{13})$-N-$R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, in which ring the nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

20. Use according to claims 14 to 16, characterised in that at least one of the substituents $R_1 - R_{11}$, preferably at least one of the substituents R_3, R_6 and/or R_9, is one of the following radicals
$-(C_1\text{-}C_4\text{alkylene})\text{-}N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})\text{-}(C_1\text{-}C_6\text{alkylene})\text{-}N^{\oplus}R_{14}R_{15}R_{16}$,
$-N[(C_1\text{-}C_6\text{alkylene})\text{-}N^{\oplus}R_{14}R_{15}R_{16}]_2$ or $-N(R_{13})\text{-}N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted $C_1\text{-}C_{12}$alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted $C_1\text{-}C_4$alkyl and/or substituted $C_1\text{-}C_4$alkyl radical and which may optionally contain further hetero atoms; or
$-NR_{14}R_{15}$, $-(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}$;,$-N(R_{13})\text{-}(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}$,
$-N[(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}]_2$ or $-N(R_{13})\text{-}N\text{-}R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, in which ring the nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

21. Use according to claims 19 and 20, characterised in that at least one of the substituents $R_1 - R_{11}$, preferably at least one of the substituents R_3, R_6 and/or R_9, is one of the radicals



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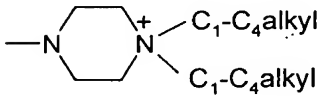
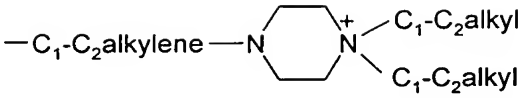


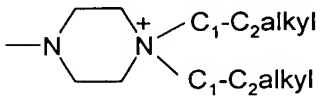
,

wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each of which independently of the other is unbranched or branched, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted.

22. Use according to claim 21, characterised in that at least one of the substituents $R_1 - R_{11}$, preferably at least one of the substituents R_3, R_6 and/or R_9, is one of the radicals



or



wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each independently of the other, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted.

23. Use according to any one of claims 1 to 22, characterised in that the metal complex compounds of formula (1) are used in washing, cleaning, disinfecting or bleaching agents.

24. Use according to claim 23, characterised in that the metal complex compounds of formula (1) are formed *in situ* in the washing, cleaning, disinfecting or bleaching agent.

25. Use according to one of claims 1 to 24, characterised in that the metal complex compounds of formula (1) are used together with peroxy compounds for the bleaching of spots or stains on textile material or for the prevention of the redeposition of migrating dyes in the context of a washing process or for the cleaning of hard surfaces.

26. Use according to one of claims 1 to 22, characterised in that the metal complex compounds of formula (1) according to claim 1 are used as catalysts for reactions with peroxy compounds for bleaching in the context of paper-making.

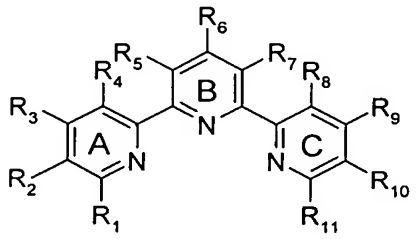
27. Use according to one of claims 1 to 22, characterised in that mixtures of manganese complexes of formula (1) with iron complexes of formula (1) are used for the prevention of the redeposition of migrating dyes and, at the same time, for the bleaching of spots or stains on textile material.

28. Use according to claim 27, characterised in that there are used mixtures of manganese complexes of formula (1) with iron complexes of formula (1'), which corresponds to formula (1) but which does not contain any quaternised nitrogen atoms.

29. Metal complex compounds of formula (1a)

$$[L_nMe_mX_p]^zY_q \qquad (1a),$$

wherein Me is manganese, titanium, iron, cobalt, nickel or copper,
X is a coordinating or bridging radical,
n and m are each independently of the other an integer having a value of from 1 to 8,
p is an integer having a value of from 0 to 32,
z is the charge of the metal complex,
Y is a counter-ion,
q = z/(charge Y), and
L is a ligand of formula (2a)



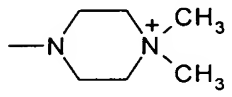
(2a),

wherein
R_6 is unsubstituted or substituted C_1-C_{18}alkyl or aryl; cyano; halogen; nitro; -$COOR_{12}$ or -SO_3R_{12} wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; -SR_{13}, -SO_2R_{13} or -OR_{13} wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; -$NR_{14}R_{15}$, -(C_1-C_6alkylene)-$NR_{14}R_{15}$, -$N^{\oplus}R_{14}R_{15}R_{16}$, -($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$NR_{14}R_{15}$, -$N[(C_1$-$C_6$alkylene)-$NR_{14}R_{15}]_2$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N[(C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$, -$N(R_{13})$-N-$R_{14}R_{15}$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together

with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, and
R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} and R_{11}, each independently of the others, has a meaning indicated above for R_6 or is hydrogen or unsubstituted or substituted aryl, with the proviso that

(i) at least one of the substituents $R_1 - R_{11}$ contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

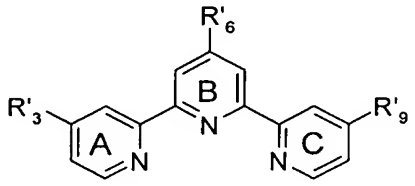
(ii) Y is neither I^- nor Cl^- if Me is Mn, $R_1 - R_5$ and $R_7 - R_{11}$ are hydrogen and R_6 is



30. Metal complex compounds according to claim 29, characterised in that Me is manganese which is present in oxidation state II, III, IV or V.

31. Metal complex compounds according to claim 29, characterised in that Me is iron which is present in oxidation state II, III or IV.

32. Metal complex compounds according to one of claims 30 and 31, characterised in that the ligand L is a compound of formula (3)

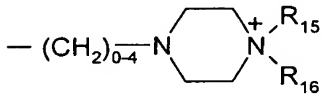


(3),

wherein

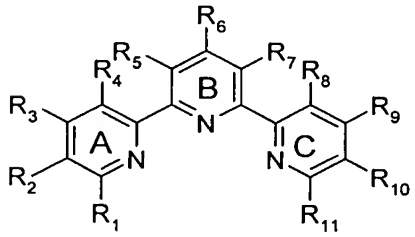
R'_6 is cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkyl-amino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy, wherein the amino groups may or may not be quaternised; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above; $-NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(CH_2)_{1-6}-NR_{14}R_{15}$, $-N(R_{13})-(CH_2)_{1-6}-N^{\oplus}R_{14}R_{15}R_{16}$,

$-N(R_{13})-N-R_{14}R_{15}$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised;
or a radical



wherein R_{15} and R_{16} are as defined above and the ring may be unsubstituted or substituted, and
R'_3 and R'_9 are as defined above or are hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above.

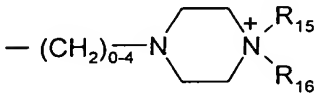
33. Compounds of formula (2b)



(2b),

wherein
R_6 is cyano; halogen; nitro; $-COOR_{12}$ or $-SO_3R_{12}$ wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-SR_{13}$, $-SO_2R_{13}$ or $-OR_{13}$ wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; $-NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(CH_2)_{1-6}NR_{14}R_{15}$, $-N(R_{13})-(CH_2)_{1-6}-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-N-R_{14}R_{15}$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, or unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted

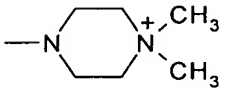
or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised;
or a radical



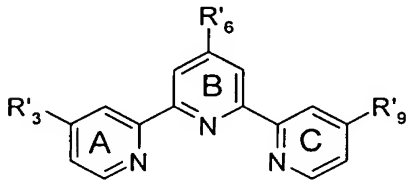
wherein R_{15} and R_{16} are as defined above and the ring may be unsubstituted or substituted, and
R_1, R_2, R_3, R_4, R_5, R_7, R_8, R_9, R_{10} und R_{11}, each independently of the others, has a meaning indicated above for R_6 or is hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl,
with the proviso that

(i) at least one of the substituents R_1 – R_{11} contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if R_1 - R_5 and R_7 - R_{11} are hydrogen and R_6 is



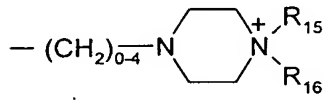
34. Compounds, according to claim 33, of formula (3)



(3),

wherein
R'_6 is cyano; halogen; nitro; -$COOR_{12}$ or -SO_3R_{12} wherein R_{12} is in each case hydrogen, a cation, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, cyano, nitro, carboxyl, sulfo, hydroxyl, amino, N-mono- or N,N-di-C_1-C_4alkyl-amino unsubstituted or substituted by hydroxy in the alkyl moiety, N-phenylamino, N-naphthylamino, phenyl, phenoxy or by naphthoxy, wherein the amino groups may or may not be quaternised; -SR_{13}, -SO_2R_{13} or -OR_{13} wherein R_{13} is in each case hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above;

$-NR_{14}R_{15}$, $-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(CH_2)_{1-6}-NR_{14}R_{15}$, $-N(R_{13})-(CH_2)_{1-6}-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-N-R_{14}R_{15}$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} may have one of the above meanings and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen, unsubstituted or hydroxyl-substituted C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above, or R_{14} and R_{15} together with the nitrogen atom linking them form a pyrrolidine, piperidine, morpholine or azepane ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical, in which ring the nitrogen atom may be quaternised;
or a radical

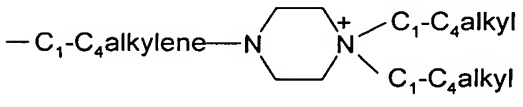


wherein R_{15} and R_{16} are as defined above and the ring may be unsubstituted or substituted, and
R'_3 and R'_9 are as defined above or are hydrogen, C_1-C_{12}alkyl, or phenyl unsubstituted or substituted as indicated above.

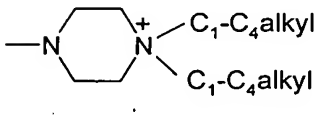
35. Compounds according to claim 32 and 34, characterised in that at least one of the substituents R'_3, R'_6 and R'_9 is one of the following radicals
$-(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})-(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}$, $-N[(C_1$-C_6alkylene$)-N^{\oplus}R_{14}R_{15}R_{16}]_2$ or $-N(R_{13})-N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is in each case hydrogen, C_1-C_4alkyl or phenyl and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms; or
$-NR_{14}R_{15}$, $-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N(R_{13})-(C_1$-C_6alkylene$)-NR_{14}R_{15}$, $-N[(C_1$-C_6alkylene$)-NR_{14}R_{15}]_2$ or $-N(R_{13})-N-R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms, in which ring at least one nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

36. Compounds according to claim 32 and 34, characterised in that at least one of the substituents R'_3, R'_6 and R'_9 is one of the following radicals $-(C_1\text{-}C_4\text{alkylene})\text{-}N^{\oplus}R_{14}R_{15}R_{16}$, $-N(R_{13})\text{-}(C_1\text{-}C_6\text{alkylene})\text{-}N^{\oplus}R_{14}R_{15}R_{16}$, $-N[(C_1\text{-}C_6\text{alkylene})\text{-}N^{\oplus}R_{14}R_{15}R_{16}]_2$ or $-N(R_{13})\text{-}N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the others hydrogen or unsubstituted or substituted C_1-C_{12}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form a 5-, 6- or 7-membered ring which is unsubstituted or substituted by at least one unsubstituted C_1-C_4alkyl and/or substituted C_1-C_4alkyl radical and which may optionally contain further hetero atoms; or $-NR_{14}R_{15}$, $-(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}$, $-N(R_{13})\text{-}(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}$, $-N[(C_1\text{-}C_6\text{alkylene})\text{-}NR_{14}R_{15}]_2$ or $-N(R_{13})\text{-}N\text{-}R_{14}R_{15}$ wherein R_{13} and R_{16} are as defined above and R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms, in which ring the nitrogen atom not bonded to any of the pyridine rings A, B or C is quaternised.

37. Use according to claim 32 and 34, characterised in that at least one of the substituents R'_3, R'_6 and R'_9 is one of the following radicals

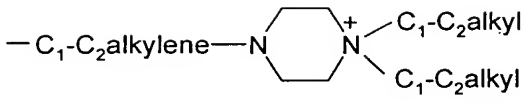


or

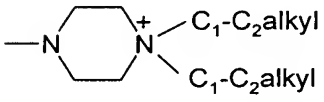


wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each of which independently of the other is unbranched or branched, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted.

38. Use according to claim 32 and 34, characterised in that at least one of the substituents R'_3, R'_6 and R'_9 is one of the following radicals

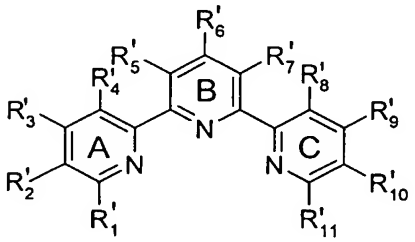


or



wherein the unbranched or branched alkylene group may be unsubstituted or substituted and wherein the alkyl groups, each independently of the other, may be unsubstituted or substituted and wherein the piperazine ring may be unsubstituted or substituted.

39. Compounds of formula (4)



(4),

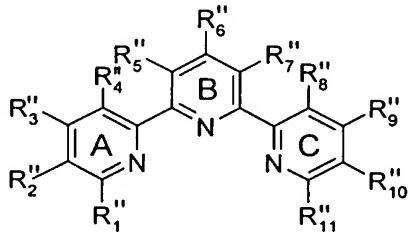
wherein

$R'_1 - R'_{11}$ are as defined for the substituents $R_1 - R_{11}$ with the exception of quaternised nitrogen atoms and with the proviso that

(iv) at least one of the substituents $R'_1 - R'_7$ is halogen, NO_2 or OR_{18}, wherein R_{18} is unsubstituted or substituted C_1-C_{18}alkyl or unsubstituted or substituted aryl and

(v) the substituents R'_8 - R'_{11} are neither halogen nor NO_2 or R_{18}, wherein R_{18} is as defined under (i).

40. Compounds of formula (4a)



(4a)

wherein R''_1– R''_{11} are as defined for the substituents R_1 – R_{11} with the exception of quaternised nitrogen atoms and with the proviso that
at least one of the substituents R''_1 – R''_7 contains a quaternisable nitrogen group which is not directly bonded to either of the two pyridine rings A and/or B.

41. Washing, cleaning, disinfecting or bleaching agents, comprising
    I) 0 - 50 % A) of an anionic surfactant and/or B) of a non-ionic surfactant,
    II) 0 - 70 % C) of a builder substance,
    III) 1 - 99 % D) of a peroxide, and
    IV) E) metal complex compounds of formula (1) in an amount which, in the liquor, gives a concentration of 0.5 – 50 mg/litre of liquor, preferably 1 - 30 mg/litre of liquor, when from 0.5 to 20 g/litre of the washing, cleaning, disinfecting and bleaching agent are added to the liquor, the percentages in each case being percentages by weight, based on the total weight of the agent.

42. Solid preparations, comprising
    a) from 1 to 99 % by weight of a metal complex compound according to claim 29;
    b) from 1 to 99 % by weight of a binder;
    c) from 0 to 20 % by weight of an encapsulating material;
    d) from 0 to 20 % by weight of a further additive; and
    e) from 0 to 20 % by weight of water.

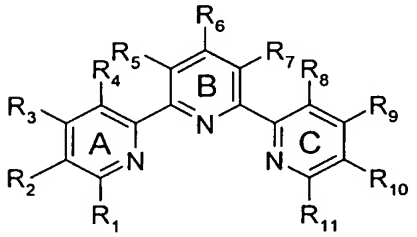
43. Solid preparations according to claim 42, characterised in that they are in the form of tablets or granules.

Abstract

Use of metal complex compounds of formula

$[L_nMe_mX_p]^zY_q$ (1),

wherein Me is manganese, titanium, iron, cobalt, nickel or copper,
X is a coordinating or bridging radical,
n and m are each independently of the other an integer having a value of from 1 to 8,
p is an integer having a value of from 0 to 32,
z is the charge of the metal complex,
Y is a counter-ion,
q = z/(charge Y), and
L is a ligand of formula (2)



(2),

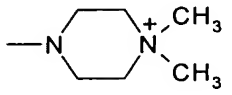
wherein

R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are each independently of the others hydrogen; unsubstituted or substituted C_1-C_{18}alkyl or aryl; cyano; halogen; nitro; -$COOR_{12}$ or -SO_3R_{12} wherein R_{12} is in each case hydrogen, a cation or unsubstituted or substituted C_1-C_{18}alkyl or aryl; -SR_{13}, -SO_2R_{13} or -OR_{13} wherein R_{13} is in each case hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl; -$NR_{14}R_{15}$, -(C_1-C_6alkylene)-$NR_{14}R_{15}$, -$N^{\oplus}R_{14}R_{15}R_{16}$, -($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$NR_{14}R_{15}$, -$N[(C_1$-$C_6$alkylene)-$NR_{14}R_{15}]_2$, -$N(R_{13})$-($C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}$, -$N[(C_1$-$C_6$alkylene)-$N^{\oplus}R_{14}R_{15}R_{16}]_2$, -$N(R_{13})$-N-$R_{14}R_{15}$ or -$N(R_{13})$-$N^{\oplus}R_{14}R_{15}R_{16}$ wherein R_{13} is as defined above and R_{14}, R_{15} and R_{16} are each independently of the other(s) hydrogen or unsubstituted or substituted C_1-C_{18}alkyl or aryl, or R_{14} and R_{15} together with the nitrogen atom linking them form an unsubstituted or substituted 5-, 6- or 7-membered ring which may optionally contain further hetero atoms,

with the proviso that

(i) at least one of the substituents $R_1 - R_{11}$ contains a quaternised nitrogen atom not directly bonded to any of the three pyridine rings A, B or C, and that

(ii) Y is neither I^- nor Cl^- if Me is Mn(II), $R_1 - R_5$ and $R_7 - R_{11}$ are hydrogen and R_6 is



as catalysts for oxidation reactions,

and also novel metal complex compounds of formula (1), novel ligands of formula (2) and starting materials therefor.